

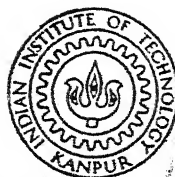
# THERMODYNAMICS OF LIQUID COPPER SILVER ALLOYS

A Thesis Submitted  
In Partial Fulfilment of the Requirements  
for the Degree of

MASTER OF TECHNOLOGY

BY

UPPAL VEERAAH CHOUDARY



DEPARTMENT OF METALLURGICAL ENGINEERING

Indian Institute of Technology Kanpur

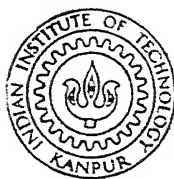
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In partial fulfilment of the requirements  
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Master of Technology in Metallurgical Engineering

by

UPPALA VEERAJAE CHOUDARY

to the  
Department of Metallurgical Engineering  
Indian Institute of Technology, Kanpur

August, 1969



CERTIFICATE

Certified that this work on "Thermodynamics of liquid Copper - Silver alloys" has been carried out under my supervision and that it has not been submitted elsewhere for a degree.



A. Ghosh

Assistant Professor

Department of Metallurgical Engineering  
Indian Institute of Technology, Kanpur

## POST GRADUATE OFFICE

This thesis has been approved  
for the award of the Degree of  
Master of Technology (M.Tech.)  
in accordance with the  
regulations of the Indian  
Institute of Technology Kanpur  
Dated. 25/8/69

### ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to Prof. A. Ghosh for suggesting this problem, for his valuable guidance and stimulating discussions the author had with him from time to time.

The author also wishes to thank

Mr. P.J. Ray Chaudhury for his active and constant help, in the construction of apparatus, during experimentation and manuscript preparation;

Mr. K. Thomas Jacob of Imperial College, London for his helpful suggestions and discussions;

Mr. K.P. Jagannathan for his timely assistance and suggestions in some of the runs;

Dr. E.S. Ray for supplying ZIRCOA-B powder and a solid electrolyte crucible;

Mr. V.P. Vohra for his help in the construction of furnace, gas train and controller unit;

Mr. V.H. Sharma for his assistance in the experimental set-up;

Mr. B. Sharma for his help in making the Zirconia-Calcia crucible.

## LIST OF CONTENTS

	PAGE NO.
LIST OF FIGURES AND TABLES	vi
LIST OF SYMBOLS	vii
SYNOPSIS	viii
CHAPTER I <u>INTRODUCTION</u>	1
II CHAPTER II <u>LITERATURE SURVEY</u>	3
II.1       Considerations of solid electrolyte galvanic cells	3
A.       Introduction	3
B.       Solid oxides as electrolytes	3
C.       Principles of electromotive force methods using solid oxide electrolyte galvanic cells	5
D.       General features of solid oxide electrolyte galvanic cells	7
D.1    Solid Electrolytes	7
D.2    Electrodes	11
D.3    Cell Assembly	13
D.4    Cell Atmosphere	15
D.5    Emf measuring devices	16
D.6    Reversibility criterion in galvanic cells	17
II.2       Applications of solid electrolyte galvanic cells	19
A.       Introduction	19
B.       Free energies of formation of simple and compound oxides - Nonstoichiometric studies	19

B.1	Simple oxides	19
B.2	Compound oxides	20
B.3	Nonstoichiometric oxides	22
C.	Activity determinations in solutions of metals and oxides	23
C.1	Solid solutions	23
(i)	Metals	23
(ii)	Oxides	25
C.2	Liquid Solutions	26
(i)	Metals	26
(ii)	Oxides	26
D.	Oxygen potentials in metal melts and gas mixtures	27
D.1	Nonferrous melts	27
D.2	Ferrous melts	27
D.3	Partial pressures of oxygen in gas mixtures	29
E.	Kinetic applications	30
F.	Miscellaneous applications	31
G.	Future Developments	32
CHAPTER III	<u>PLAN OF THE WORK</u>	33
A.	Previous work on Cu-Ni system	33
B.	Plan of the present work	35
CHAPTER IV	<u>APPARATUS &amp; EXPERIMENTAL TECHNIQUES</u>	39
A.	Furnace and Reaction Tube	39

B.	Temperature Control & Measurement	40
C.	Emf measurement	40
D.	Gas Train	40
E.	Experimental Materials	41
F.	Cell Assembly	42
G.	Calibration Runs	45
I.	Experiments on Cu-Ag system	47
CHAPTER V	<u>RESULTS &amp; DISCUSSIONS</u>	50
A.	Results	50
B.	Discussions	52
CHAPTER VI	<u>SUMMARY &amp; CONCLUSIONS</u>	56
CHAPTER VII	<u>SUGGESTIONS FOR FURTHER WORK</u>	57
APPENDIX		
A.	Emf data	69
B.	Computer programme for calculating partial molar values of copper in Cu-Ag alloys	77
C.	Preparation of solid electrolyte crucibles	78
D.	Estimation of oxygen solubility in liquid Cu-Ag alloys	80
E.	Uncertainty Analysis	82

## BIBLIOGRAPHY

84

1.	<u>(Copper - silver system; Thermodynamics of metallic solutions - Solution models - Phase diagram correlations)</u>	84
2.	<u>(Solid electrolytes - classified references according to various metallurgical applications)</u>	87
A.	Reviews & General References	87
B.	Physical Properties	88
C.	Thermodynamics of Binary and Compound Oxides - Nonstoichiometry	90
D.	Activity determinations in liquid and solid solutions of metals & oxides	93
E.	Oxygen potentials in metal melts & gas mixtures	95
F.	Kinetic Applications	97
G.	Determination of diffusion coefficients	98
H.	Miscellaneous Applications	99

# LIST OF FIGURES & TABLES

## FIG. NO.

1. Cell Assembly
2. Experimental data of electromotive force versus temperature for liquid Cu-Ag alloys.
3. Activity plots in liquid Cu-Ag alloys
4.  $\alpha$  function for Cu in liquid Cu - Ag alloys
5.  $\beta$  function for Cu in liquid Cu - Ag alloys
6. Integral molar heats and entropies of mixing in liquid Cu - Ag alloys
7. Integral and excess molar free energies of mixing in liquid Cu - Ag alloys
8. Copper-Silver phase diagram

## TABLE NO.

1. Temperature dependance of emf for the calibration cell Ni, NiO/CaO -  $\text{ZrO}_2$ /Cu,  $\text{Cu}_2\text{O}$ .
2. Experimental data on liquid Cu - Ag alloys
3. Activities in liquid Cu - Ag alloys
4. Thermodynamic functions of mixing at 1300°K in liquid Cu - Ag alloys.

LIST OF SYMBOLS

$A, E$	- Metals
$C, D$	- Empirical constants
$a_i$	- Activity of $i$ th component
$e_M^O$	- Interaction coefficient of oxygen with metal $M$ in the melt
$E$	- Electromotive force, mV
$f^O$	- Activity coefficient
$F$	- Faraday constant, kcal/mV equivalent
$F_i^M$	- Relative partial molar free energy of mixing, of $i$ th component, cal/g-atom
$H_i^M$	- Relative partial molar enthalpy of mixing of $i$ th component, cal/g-atom
$S_i^M$	- Relative partial molar entropy of mixing of $i$ th component, cal/ $^{\circ}$ K g-atom
$F^M, H^M, S^M$	- Integral molar properties of mixing
$F^E, S^E$	- Excess molar properties of mixing
$K$	- Equilibrium constant, atm $^{-1}$
$P_{O_2}$	- Partial pressure of oxygen, atm
$R$	- Universal gas constant, cal/ $^{\circ}$ K mole
$T$	- Temperature, $^{\circ}$ K
$X_i$	- Mole fraction of $i$ th component
$\alpha_{Cu}$	- Alpha function for copper
$\beta_{Cu}$	- Beta function for copper
$\gamma_i$	- Activity coefficient of $i$ th component
$\Delta F_{\text{fusion}}$	- Free energy of fusion of copper, cal/g-atom
$\Delta S_{\text{fusion}}$	- Entropy of fusion of copper at 1356 $^{\circ}$ K, cal/ $^{\circ}$ K g-atom

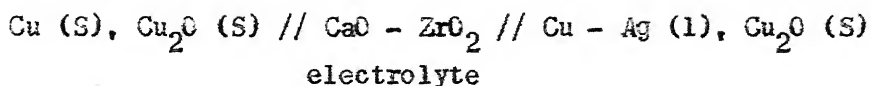


## SYNOPSIS

### THERMODYNAMICS OF LIQUID COPPER - SILVER ALLOYS

U.V. CECUDARY

The reversible galvanic cell:



was employed to determine the thermodynamic properties of the liquid copper-silver alloys in the range of  $X_{\text{Cu}}$  from 0.1 to 0.8 and temperature from liquidus to 1330°K. The liquidus temperatures of silver-rich alloys determined from the few measurements did not match with the phase diagram values. The activities of copper were found to be higher than the values reported by Hultgren et al in the silver-rich side, whereas they agree well in the high copper side,  $F^{\text{H}}$  and  $F^{\text{E}}$  values obtained by extrapolation of data in this study agree well with those reported in literature.  $E^{\text{H}}$  values of this study agree with the calorimetric results within the experimental uncertainty. Small values of  $S^{\text{E}}$  of this work, confirm the nearly regular behaviour of Cu - Ag system.

## INTRODUCTION

A knowledge of thermodynamic properties of metallic solutions is extremely useful for the understanding of various metallurgical processes. For instance, thermodynamic data are needed to formulate the conditions of equilibrium between the alloys and a gas phase or slag. Also, thermodynamic data give a quantitative basis for better understanding of the peculiarities of phase diagrams and constitution of various metallic phases. Solutions of interest to the metallurgist can be binary, ternary or more complex containing number of components. To understand the nature of complex solutions, basic thermodynamic data of binary solutions will be of great help. At present data are available for barely 200 binary systems out of the 3000 and odd possible systems. Even amongst these well studied systems, the thermodynamic properties are some times known with less precision and more accurate data are needed.

Thermodynamic investigations usually consist of experimental determination of either the integral molar enthalpy of mixing or heat capacities by calorimetric methods or the partial molar free energies utilizing the various equilibrium measurements, such as electromotive force, vapor pressure, chemical reaction equilibria and distribution equilibria. Equilibrium methods afford the direct determination of free energies of mixing and the

activity values in some systems <sup>are</sup> known with less than 2% uncertainty.

Electromotive force methods and vapor pressure measurements are more popular among the equilibrium methods, and more than 75% of the binary systems were studied by these methods. For activity determinations the equilibrium methods are considered more reliable than the calorimetric methods.

Literature survey revealed that the thermodynamic properties of Cu-Ag system are in error. Hence it was decided to investigate the thermodynamics of Cu-Ag system by electromotive force (emf) method using solid electrolyte. This technique has already been established as one which is capable of yielding accurate results.

## CHAPTER II

LITERATURE SURVEYII. a. Considerations of solid electrolyte galvanic cells.A. Introduction:

Solid electrolytes can be considered as solid inorganic compounds or phases with well defined crystalline structure and exhibiting ionic conduction in a considerable ranges of temperature and chemical potentials of metal or non-metal conducting species. Though various solid electrolytes such as halides and oxides were used right from the beginning of this century, keen interest was evinced in solid electrolyte galvanic cells only after the classic work of Kulkola & Wagner (42) in this field. A host of papers published in the last ten years, bringing forth the various applications of solid electrolytes, stand testimony to the versatality of these. Mostly solid oxide electrolytes have been used in a variety of metallurgical investigations undertaken in the recent years and hence complete attention will be devoted to the oxide solid electrolytes.

B. Solid oxides as electrolytes:

The total electrical conductivity of the solid electrolytes may be expressed as the sum of three terms

where  $\sigma_{ion}$ ,  $\sigma_{eh}$  and  $\sigma_e$  refer to the conductivities of ions, electron holes and electrons in the electrolyte.

Electrical conductivity of these oxides vary as a function of temperature and partial pressure of oxygen ( $P_{O_2}$ ) prevailing over the oxides. Below a critical partial pressure, conductivity due to electrons becomes significant whereas above an upper limit of  $p_{O_2}$ , electron hole conduction predominates. In the intermediate range of oxygen partial pressures, conductivity is constant with temperature and is primarily due to the ions alone. If an oxide has to be used as electrolyte in a solid electrolyte galvanic cell, its conductivity should be almost wholly due to oxygen ions, i.e., transport number of oxygen ions  $t_{O^{2-}}$  should be close to unity, in the temperature and partial pressure ranges of interest. Simple binary oxides with few exceptions like  $BeO$ (73) and  $SiO_2$ (44) ~~are~~ found to be unsuitable because of their considerable electronic conduction. Some of the oxides eg:  $Al_2O_3$  (44,71,144),  $MgO$  (44,59,144) and rare earth oxides (44,74,111) exhibit complete ionic conduction only in a very narrow ranges of temperature and  $p_{O_2}$ . Hence they are of little interest in many applications involving solid electrolytes.

For extending the ranges of temperature and  $p_{O_2}$  in which  $t_{O^{2-}}$  is almost unity, doping of the simple binary oxides with aliovalent oxides have been found to be of immense help. Especially the solid solutions of tetravalent oxides  $ZrO_2$ ,  $ThO_2$  or  $HfO_2$  with lower valent oxides  $CaO$ ,  $Y_2O_3$ ,  $Y_2O_3$  or  $MgO$  have received increasing

attention over the years. These have fluorite ( $\text{CaF}_2$ ) type structure with oxygen ion defects resulting from the substitution of lower valency cations  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{La}^{3+}$ , or  $\text{Y}^{3+}$  for the tetravalent  $\text{Zr}^{4+}$ ,  $\text{Th}^{4+}$  or  $\text{Hf}^{4+}$ . Hund (56) and D. Roy & R. Roy (67) reviewed the various types of solid solutions formed when a fluorite type solvent is doped with aliovalent cations. Extensive conductivity measurements on these solid solutions, under varied conditions of  $p_{\text{O}_2}$  and temperature, helped in the diagnosis of electronic conduction limits and establishment of the 'ionic plateau'. Out of various solid solutions with fluorite structure, calcia-stabilized zirconia and yttria stabilized thoria have been more popular due to their exclusive ionic conduction in a wide spectrum of oxygen partial pressure. Various studies (42,43,47,48,66,74,76, 137 e, 138,144,145,148) employing doped zirconia and doped thoria have clearly established the temperature and  $p_{\text{O}_2}$  limits for ionic conduction ( $t_{\text{O}_2} > 0.99$ ).

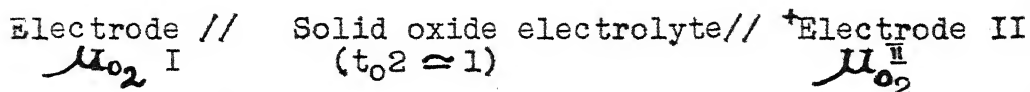
C. Principle of electromotive force (emf) methods using solid oxide electrolyte galvanic cells:

From the first and second laws of thermodynamics, free energy change for a reversible process is given by

$$dF = VdP - SdT - \delta w' \quad (1)$$

$dF$  is the Gibbs free energy change;  $V, P, S, T$  have usual significance; and  $w'$  is the work done by the system other than that against pressure. At constant temperature and pressure above Eq. reduces to  $dF = -\delta w'$  (2)  
on intergration, we have  $\Delta F = -W'$  (3)

In the galvanic cell the work to be considered is the electrical work done when transport of charge takes place from one potential to another. Consider the following galvanic cell:



The emf of above galvanic cell results from the difference in chemical potentials of oxygen  $\mu_{O_2}^I$  &  $\mu_{O_2}^{II}$  at the left and right electrodes. Assuming that the oxygen ions are the chief conducting species in the electrolyte, the emf of the above galvanic cell can be related to the free energy change of the cell reaction  $O_2(II) = O_2(I)$  (4)

If the emf of the cell is  $E$  volts and the reaction taking place is accompanied by passage of  $n$  Faradays is  $nF$  coulombs, the work done by the system in the cell is  $nFE$  volt coulombs. Therefore, according to the eq.(3)

$$\Delta F = \mu_{O_2}^I - \mu_{O_2}^{II} = -nFE \quad (5)$$

Since the reaction (4) takes place by passage of 4 faradays,  $n=4$ . If  $\mu_{O_2}^0$  and  $p_{O_2}^0$  represent the chemical potential and partial pressure of oxygen, Eq. (5) can be written as

$$(\mu_{O_2}^0 + RT \ln \frac{p_{O_2}^I}{p_{O_2}^0}) - (\mu_{O_2}^0 + RT \ln \frac{p_{O_2}^{II}}{p_{O_2}^0}) = -4FE \quad (6)$$

where  $p_{O_2}^I$  &  $p_{O_2}^{II}$  are equilibrium oxygen partial pressures at left and right side electrodes;  $R$  is gas constant;  $T$  is the absolute temperature.

Simplifying Eq.(6)

$$E = \frac{RT}{4F} \ln \frac{p_{O_2}^{II}}{p_{O_2}^I} \quad (7)$$

usual convention of cell emf is adopted - the cell emf is taken as positive when positive current flows through external circuit from right to left. If oxygen potential or  $p_{O_2}$  is known at one electrode, oxygen potential at the other electrode can be calculated from the cell emf, using eq.(7)

#### D. General features of solid oxide electrolyte galvanic cells:

A galvanic cell assembly consists of an electrolyte with appropriate electrodes in close contact with the electrolyte. Lead wires in contact with the electrodes act as pure electronic conductors and emf developed as a result of cell reaction can be measured by a convenient potential measuring device. To measure meaningful emf's, various features of the galvanic cell have to be analyzed. Main considerations in the setting up of galvanic cell are discussed below.

##### D.1 Solid electrolytes:

Solid electrolytes can be used successfully in various applications, provided they satisfy certain prerequisites.

(i) They should have high thermodynamic stability at high temperatures. These should not undergo any transformation in the experimental temperature range.



(ii) For certain applications such as oxygen determination in steel making, the solid electrolyte should possess high thermal shock resistance. Either by altering the composition of the stabilizing agent or using altogether different electrolytes, desired thermal shock resistance have been achieved without making much compromise to the ionic behaviour of the electrolyte. Diaz and Richardson (143) have reported that 7 mol% lime stabilized zirconia has superior thermal shock resistance than the more popular 15 mol% composition, at the same time exhibiting satisfactory ionic conduction.

(iii) Solid electrolytes should be impervious to gases and should have as high a density as possible. Single crystal specimens of electrolyte are well suited because of their high purity, high density and low surface area. Many of the solid electrolytes in use are difficult to get in single crystal form. Pressed and sintered pellets, crucibles or tube shapes served the purpose. High density and impermeability to gases is achieved by employing maximum possible sintering temperature, as high as 2200°C.

(iv) Solid electrolytes should exhibit predominant oxygen ion conduction and negligible electronic conduction under experimental conditions of temperature and partial pressures. For conditions of complete ionic conduction ( $t_{O_2} > 0.99$ ), the simple relation between the

emf of the cell and the free energy of the reaction,

$F = - nFE$  is valid. But if electronic conductivity is appreciable ( $T_e \approx 0.01$ ), knowledge of  $t_{O_2}$  as a function of chemical potential of oxygen is essential to relate the cell emf and the free energy change. Under these conditions, it can be shown that (52)

$$E = \frac{1}{4F} \int_{\mu_{O_2}^I}^{\mu_{O_2}^{II}} t_{O_2} d\mu_{O_2} \quad (8)$$

An accurate evaluation of the above integral is rendered difficult due to the lack of precise knowledge of variation of  $t_{O_2}$  with oxygen potential ( $\mu_{O_2}$ ). However, if an electrolyte with mixed conduction has to be used for a particular application, two approaches can be followed for evaluating the above integral. Analytical approach to the above problem has been suggested by Schmalzried (44). By the introduction of two parameters  $P_{\sigma}$  and  $P_{\sigma_0}$  which are defined as the oxygen partial pressures at which  $\sigma_{O_2}$  equals  $\sigma_{\sigma_0}$  and  $\sigma_{\sigma}$  respectively, he derived  $t_{O_2} - p_{O_2}$  relationships for various types of electrolyte systems. Second approach is due to Rapp (74), which is essentially a graphical integration of the above equation from the plot of  $t_{O_2}$  vs chemical potential of oxygen.

An analysis of the problems arising from electronic conduction and theoretical derivation of cell emf under conditions of mixed conduction can be found in the papers by Steele (102), Schmalzried (44), Pal'guev. et al (43) and

Rapp (74). Aforementioned approaches are valid only if internal 'short circuiting' behaviour of electronic conductivity is not detrimental to stability of the cell emf with time. When the electronic conductivity is considerable, oxygen is continuously transferred from higher oxygen potential electrode to lower oxygen potential electrode. Unless the relevant electrochemical reactions and mass transport processes are rapid, the flux of oxygen may disturb the oxygen potential at the electrodes resulting in either lower cell emf or continuous decrease in cell emf till it drops down to zero (102).

(v) Solid electrolytes should be chemically unreactive to the electrodes employed and the cell reaction at the electrode-electrolyte interface should be unambiguous and clearly defined. The local thermodynamic equilibrium at the interface is affected if there is dissolution of electrode components or chemical compound formation as a result of chemical reaction between the electrolyte and electrode. These may bring about change in relative concentrations of electrode constituents or affect the kinetics of relevant electrochemical reactions and hence produce erroneous emf values. Normal reversibility tests employed to test the performance of the cell will be useful in detecting the deviations of the cell from reversible behaviour.

No single electrolyte may satisfy all the above requirements. Therefore one has to choose the electrolyte with care.

#### D.2 Electrodes:

Electrodes can be solid, liquid or gaseous. One of the electrodes in the galvanic cell is of known oxygen potential and is usually termed as the reference electrode. The electrodes should be quite reversible and have as much 'oxygen buffer capacity' as possible to guard them against possible polarization effects and minor side reactions. Among solid electrodes, Fe-FeO mixture is shown to be highly reversible(102). Usual preparation of solid electrodes consist of thoroughly mixing the electrode mixture pressing them into compacts and sintering them at the desired temperature. Since electrode mixture contains either two or more phases (metal-metal oxide or two oxide mixtures), powders employed should be as fine as possible to allow rapid equilibration in the electrolyte. If either crucible or short tube electrolytes are used, the finely ground electrode mixture can be sintered 'insitu' inside the electrolyte. The lead wires commonly employed are platinum wires welded to a platinum disks well pressed against the two electrodes. If different lead wires are used, the thermoelectric potential of the two leads must be determined and necessary corrections should be made to the cell emf.

Liquid electrodes consist of either liquid metal in equilibrium with its oxide (134) or liquid metal with a known amount of oxygen dissolved in it (141,143). As a rule, liquid electrodes perform better than solid electrodes provided there are no ~~corrosive~~ effects on the electrolyte employed. Electrolyte used is in the form of crucible or tube which serves as container for one of the electrodes. The leads used should dissolve as little as possible in the electrodes. Leads can be either be dipped momentarily during the time of emf measurement or continuously immersed if the solubility of the lead in the electrode is negligible. For instant dipping Ta (141), Mo (142), Pt (12,137), stainless steel (143), ~~Ir~~ (134), Ni-coated with NiO (116) and many others were used whereas for constant immersion, sintered oxides such as  $\text{Cr}_2\text{O}_3$  (142) and cermets (137,143) were preferred. Continuous dipping of lead is recommended though instant dipping leads will give accurate emf in the absence of dissolution reaction accompanied by spurious emf. For solid electrolyte applications above  $1600^\circ\text{C}$ , liquid metal with oxygen dissolved, low enough not to form an oxide, is highly suitable to avoid the ~~corrosive~~ effects of oxide on the solid electrolyte (52,P 56).

Gaseous electrodes consist of gas mixtures of either known or unknown oxygen potential, flowing over supporting electrode such as Pt in close contact with electrolyte tube (55, 128, 138, 143, 148). These electrodes are convenient, provided there is no leakage between the two electrodes of the galvanic cell. These are often better than solid electrodes where various interface deteriorations may develop during operation of the cell.

### D.3 Cell assembly:

Various designs of cell assembly are possible and the choice of particular design is dictated by the system being investigated. The earliest investigations using solid electrolyte galvanic cell for determination of free energies of formation of oxides, were done by Kiukkola & Wagner (42). They employed "open cell stacked pellet-technique" wherein the solid electrodes were kept firmly pressed to either side of the electrolyte and the cell was operated under a flow of inert gas. This kind of simple cell assembly has been found to be adequate for high oxygen potential systems but proved to be unreliable for investigations involving low oxygen potential systems. Also a gas transport from one electrode to another is a serious problem in this simple cell assembly, possibly resulting in mixed potentials. Various improvements have been effected in the latter cell designs by

Carter (110); Schmalzried (81,111); Goto & Matsushita(46); Steele & Alcock (47) and Charette & Flengas (108). In all these designs, attempts have been made to promote local thermodynamic equilibrium by keeping loose electrode mixture around the electrodes and also by providing individual compartments for the electrodes with separate inert gas streams. Steele & Alcock (47) tried to achieve this by pressing two polished alumina tubes to the electrolyte surface on each side with separate gas stream in each tube. Intermixing of gas streams of the two electrodes cannot be completely ruled out in this kind of design. Charette & Flengas (108) used hermetically sealed half cell compartments with large amounts of electrode mixtures and operated the cell in vacuum. This improved design gave rapid cell response and stable emf's could be recorded over periods of even several weeks. For liquid systems, solid electrolyte crucibles can be employed if the particular geometry does not affect the cell emf by way of gas transport. Galvanic cell assemblies with crucible electrolytes were successfully used by various investigators (116,123,126,134). If one of the electrodes is gaseous or the gas transport problem is acute, one end closed electrolyte tubes with separate gas streams can be employed. Many emf measurements (123,125,133,137, 139-144) have been made in molten metals and gas mixtures using the tubular geometry. Since the cost of the tube electrolytes is too prohibitive for routine applications

(eg: oxygen monitoring in steels). A disk electrolyte sintered to one end of quartz tube has been developed (138,148). These are good for instantaneous oxygen determinations in molten metals and can be discarded whenever a failure in the electrolyte occurs. Electrolyte discs can be cemented to a supporting tube such as alumina. If the seal between the disk electrolyte and supporting tube is good it can be used for oxygen partial pressure measurements in gas mixtures. Such an oxygen gauge has been successfully devised by Weissbart & Ruka (128). Attention should be paid to the constancy of temperature across the cell assembly. This can be taken care of by using a furnace of considerable constant temperature zone or alternatively making the cell assembly as small as possible. In the presence of temperature gradient across the cell, thermal emf should be taken into account for precise interpretation of cell emf's. Also, the cell assembly should be surrounded by a grounded metal sheath so as to avoid the spurious emfs arising from furnace windings and ancillary control equipment.

#### D.4 Cell atmosphere:

In many applications, galvanic cell measurements are made either under vacuum or inert atmosphere. Purified He, Ar or N<sub>2</sub>, devoid of either oxidizing or reducing impurities, can be used for this purpose. By successively passing the gas through one or more of the furnaces



with Cu turnings, Mg chips, Ti sponge or Zr-Ti alloys, traces of oxygen and hydrocarbons in the inert gas can be removed to quite an extent. Moisture and  $\text{CO}_2$  can be eliminated with the help of  $\text{CaCl}_2$ ,  $\text{P}_2\text{O}_5$  and liquid oxygen traps. To prevent the accumulation of released impurities in the vicinity of the cell, dynamic vacuum or flowing stream of purified gas is preferred. While operating the cell under vacuum, special trap to prevent the back diffusion of pump vapors should be set up. Steele & Alcock (47) have obtained the same emf values under inert gas flow as well as vacuum, demonstrating that there are no special advantages in the use of vacuum. To minimize mixed potentials, independently purified gas streams after prior equilibration with the electrode mixture, should be admitted into separate compartments of the galvanic cell.

#### D.5 Emf measuring devices:

Open circuit emf of the galvanic cell can be measured by a variety of devices-potentiometer, oscilloscope bridge\*, valve voltmeter<sup>(102)</sup> or electrometer (102,143). Potential measuring device should pass as little current as possible through the cell without causing undue polarizations at the electrodes. Care should be taken while measuring emf by oscilloscope bridge and electrometers as these are more susceptible to extraneous emf pickup. If the resistance of the electrolyte is not too high (usually

\* Activities in molten alloys - EMF methods) - K. OKAJIMA & H. SAKAO  
J.JAP. INST. METALS, 9, 47, 1968.

above  $800^{\circ}\text{C}$ ), potentiometer is preferred. For cells with higher resistances, other devices like vibrating reed electrometer will be a better choice(102). Emf measurements were reported to a temperature as low as  $350^{\circ}\text{C}$  , using the electrometer (103).

#### D.6 Reversibility criterion in galvanic cells:

Once the galvanic cell is in operation, reversibility of the cell emf has to be demonstrated by disturbing the local thermodynamic equilibrium. Reversible behaviour of the cell can be established by the following checks.

(i) A small amount of current, of the order of microamperes is passed through the cell first in one direction and next in the opposite direction, for at least half an hour. The cell becomes polarized and initially either decrease or increase in cell emf is noticed depending on the direction in which current is passed. The cell emf is observed with time and the quick stabilization of emf denotes good reversible behaviour of the cell. Solid systems are more ~~prone~~ to polarization effects and hence take considerably long time to reach equilibrium.

(ii) After equilibrating the cell at a particular temperature, the stability of emf with time should be observed over a period of twelve hours. The constancy of emf during this period, indicates possible reversibility of the cell.

(iii) Reproducible emf should be observed at the same temperature in both heating and cooling cycles of the cell. At least one temperature excursion should be done.

(iv) Flow rate of the gas stream can be varied and its effect on cell emf should be studied. If the emf is stable for a reasonable variations of flow rate, it can be considered reversible provided preceding checks also confirm this. Also small amounts of gaseous impurities can be injected in the gas stream and the quick return of emf to equilibrium indicates reversibility.

## II.2 APPLICATIONS OF SOLID ELECTROLYTE GALVANIC CELLS

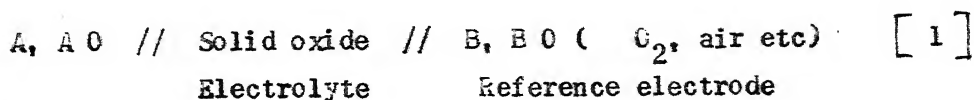
### A. Introduction

Solid electrolyte galvanic cells have been useful in obtaining precise thermodynamic data for various metal oxides, solutions of metals or oxides. Also, accurate studies of number of new alloy systems and nonstoichiometric compounds have become possible. Continuous measurement of oxygen contents in liquid metals and in various gas mixtures has led to new control methods in various metallurgical industries. Various other applications include the determination of phase boundaries, diffusion coefficients of oxygen in solid and liquid metals and corrosion behaviour of materials. Numerous kinetic studies such as rate of deoxidation of steels, rates of oxidation and reduction of metals and metal oxides have been done in the recent years. Principles of most of these applications are outlined below.

### B. Free energies of formation of simple and compound oxides - Nonstoichiometric studies :

#### B.1 Simple oxides

Free energies of formation ( $\Delta F^0$ ) of various metal oxides can be accurately determined from the reversible emf of the cells of the type



The emf can be thought to be either due to the displacement reaction



or due to the oxygen potential difference on either side of the electrolyte

$$\frac{1}{2} O_2 (A, A O) = \frac{1}{2} O_2 (\text{Ref. electrode}) \quad (2)$$

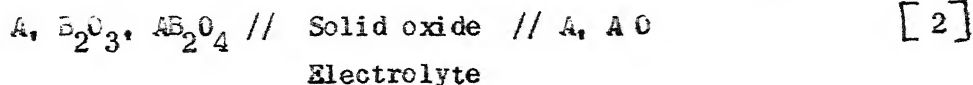
If the oxygen potential in the reference electrode is fixed either by controlled gas mixtures or with a metal and metal oxide of known free energy of formation (BO in cell), the free energy of formation of unknown metal oxide can be accurately determined from the reversible cell emf using the relation

$$\Delta F_{BO}^O = \Delta F_{AO}^O - n F E \quad (3)$$

Various metal oxides (when A, B = Cu, Pb, Ni, Co, Sn, Ec, Mn, Mo, Cr, U, V, W, Nb) have been studied (42, 43, 46, 47, 88, 92, 95, 99, 100, 107) by this technique. Since the cell emf's can be measured to an accuracy better than 1 millivolt in many cases, the overall uncertainty in the free energies of formation can be reduced to 100 calories per mole of oxygen.

### B.2. Compound oxides

Free energy of formation of a variety of compound oxides such as spinels (81, 84, 89, 93, 105), silicates (93), molybdates (105), tungstates (83) have been determined using the galvanic cell of the type



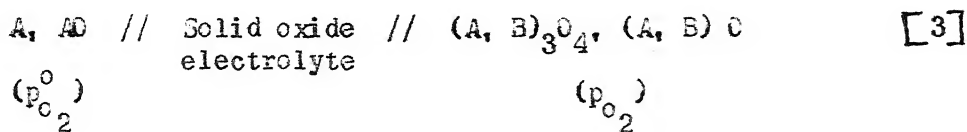
Overall reaction can be considered as



$$\Delta F_{AB_2O_4}^O = - n F E \quad (5)$$

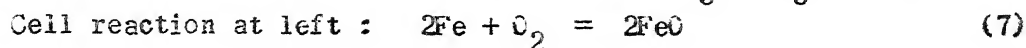
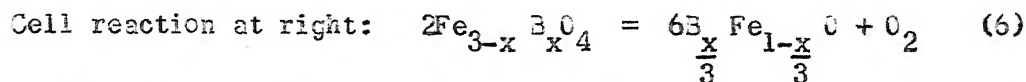
Precautions have to be taken to ensure reversible electrode reaction in this kind of cells. The equilibration of oxide phase mixtures is sluggish and hence intimate mixture of the oxide phases has to be prepared by repeated grinding and sintering at suitable high temperatures. Since a stable cell emf requires a passage of small amounts of current to result in presumed equilibrium cell reaction, ionic reaction components in oxide phase mixtures should have high enough mobility to establish the necessary local thermodynamic equilibrium.

An interesting variation of the galvanic cell is used to measure the dissociation pressures of two phase mixed spinel-wustite composition  $(A, B)_3O_4 - (A, B) O$  and the cell can be depicted as



Such studies have been carried out on a number of spinel solid solutions of the type  $(Fe, B)_3O_4$  where  $B = Ni, Mg, Mn, Co$  (86, 110, 115). The cell was set up with the prepared composition of  $(Fe, B)_3O_4$  solid solution spinel phase on the right side and the current was passed to reduce the spinel. The cell reaction is the oxygen transport from right to left side of the electrolyte. If the reduction product were wustite of same  $Fe : B$  ratio, the cell emf would be invariant to further passage of moderate amounts of

current once the small initial current had been passed to establish the second phase. This was observed in the case of spinel solid solution range  $\text{Fe}_3\text{O}_4$  to  $\text{Fe}_{2.4}\text{Co}_{0.6}\text{O}_4$ , by Carter (110).



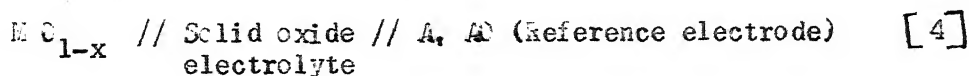
Dissociation pressures of spinel solid solution ( $p_{\text{O}_2}$ ) is given by the relation

$$\ln p_{\text{O}_2} = \ln p_{\text{O}_2}^0 - \frac{nFE}{RT} \quad (8)$$

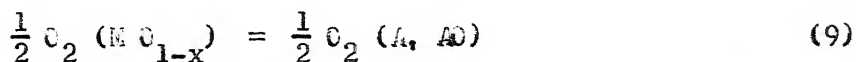
Free energy of formation of  $(\text{Fe}, \text{B})_3\text{O}_4$  can be calculated provided activity values of  $\text{BO}$  and  $\text{FeO}$  in  $\text{Fe}_{1-\frac{x}{3}}\text{B}_{\frac{x}{3}}\text{O}$  solid solutions are known.

### B.3 Nonstoichiometric oxides

Nonstoichiometry in oxides such as  $\text{UO}_2$ ,  $\text{UO}_2 - \text{TiO}_2$ ,  $\text{PuO}_2$  (80, 91, 96, 103);  $\text{TiO}_2$  (90, 101, 105);  $\text{NbO}_2$  (85, 101, 95);  $\text{MoO}_2$  (101) and  $\text{WO}_2$  (99) have been studied using the cells of the type:



Reaction is



These studies are helpful in establishing the phase boundaries between the phase mixtures and single phase solid solutions of oxygen in metal oxides.

The knowledge of the partial molar free energy of oxygen ( $\Delta \overline{\text{Fe}}_2$  of  $\text{Fe}_2$ ) in  $\text{M} - \text{O}_2$  system helps in assessing the minimum amount of contaminating oxygen

that will be present in the extractive metallurgy of various reactive metals Nb, U, V etc. Since the nonstoichiometric oxides are easily affected by cell atmosphere, the atmosphere should be extremely pure. Separate compartment cells in which individual streams of purified gas pre-equilibrated with the electrode mixture under study have been advocated.

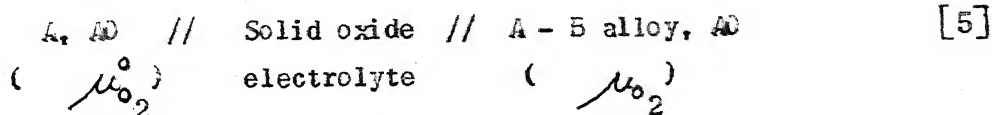
The nonstoichiometric oxides can be prepared by partial oxidation or reduction of stoichiometric oxides employing gas handling systems or by coulometric titration of oxygen into or out of the oxide of known composition. Coulometric titration consists of imposing an external emf on the cell so that known amount of current is passed for a certain time. From this the amount of oxygen transferred into (or out of) the nonstoichiometric electrode is known and hence new composition of the electrode can be fixed. To study narrow ranges of stoichiometry where conventional methods of gas equilibration fails, this method is extremely useful. Applicability of various defect models to these nonstoichiometric oxides can be assessed. Studies of Hoch (85) and Schmalzried (106) point out to such possibilities.

### C. Activity determinations in solutions of metals and oxides

#### C.1 Solid solutions:

##### (i) Metals:

Oxygen concentration cells of the type





can be used for the determination of activities and phase boundaries in binary metallic solutions. Though such measurements are possible in ternary solutions, so far none have been reported.

$$\text{Cell reaction: } \underline{O} (A-B \text{ alloy}, A) = \underline{O} (A, AO) \quad (10)$$

$$\text{or } A = \underline{A} (B)$$

$$\mu_{\underline{O}_2}^0 - \mu_{O_2} = - n_{EF} \quad (11)$$

Since chemical potential of metal A is related to that of oxygen through the equilibrium constant for the formation of AO ( $A + \underline{O} = AO$ ), emf of the cell can be related to the activity as follows :

$$RT \ln a_A = \mu_A - \mu_A^0 = \frac{1}{2} (\mu_{\underline{O}_2}^0 - \mu_{O_2}) = - 2EF \quad (12)$$

By measuring the cell emf as a function of temperature and composition, activities in the binary system can be determined. From these data, various other thermodynamics properties of the system can be calculated.

For satisfactory operation of the cells, additional conditions besides the usual ones mentioned in Ch. II.1, should be met. These are noted below.

Oxygen solubility in A and AO should be as small as possible so that activity of A and AO can be taken as unity. Also, solubility of oxygen in A-B alloy should be small. If the oxygen solubility is appreciable, the activities determined would not correspond to a true binary system A-B. A should be pure and stoichiometric. B should be more noble than A i.e. the free energy of formation of AO must be quite more negative than that of BO. It should differ by a minimum of 10 Kcals (116), so as to

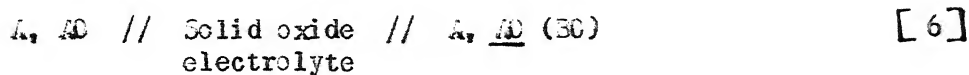
avoid the displacement reaction:  $AO + B = A + BO$

$A + B \rightarrow A + B$ , which results in compositional changes.

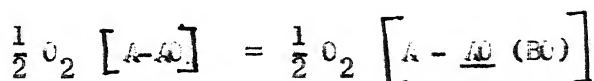
Solid systems Cu - Ni (112); Fe-Au, Fe-Pt, Fe-Au, Co-Au (114-121); Co-Mo, Co-Pt (113); Au-Ni (120); Cu-Pt (119); Ta-W, Ta-Mo (124); Cr-Ni, Co-Pt (125) have been studied by solid electrolyte technique. Also activities of Co in Co<sub>3</sub>W (113) and Ga in Ni-Ga (117) have been determined. This technique helps in determining the phase boundaries from the break in emf vs. temperature plots. Accurate estimates of solidus lines have been made in Cr-Ni and Co-Pt systems, by Fitterer et al (125) and consistency with the established phase diagrams is reported for Fe-Au and Co-Au systems by Kubik and Alcock (121).

#### (ii) Oxides:

The activity of oxides in solid solutions can be derived from the emf of the cell



Cell reaction



$$\text{or } AO = \underline{AO} (BC) \quad (13)$$

Considerations are analogous to that stated in (i) and activity of AO is given by

$$a_{AO} = \exp \left( -\frac{4 EF}{RT} \right) \quad (15)$$

Activities of FeO in FeO-MgO solid solutions (115) and that of NiO in NiO-MnO and NiO-MgO (122) have been determined using this technique.

## C.2 Liquid solutions

Measurements of activities in liquid solutions are comparatively few. The increased solubility of the oxygen in the liquid solutions and corrosiveness of these solutions limit the applicability of emf measurements to very few systems.

### (i) Metals:

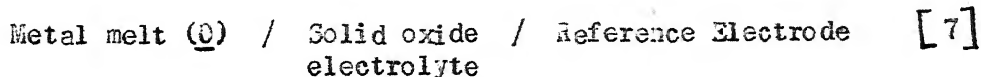
Activity determinations in liquid metals do not differ in principle from that of solid solutions. Cell assembly design is different for liquid solutions and operating temperature is fairly high. Since high oxygen solubilities contaminate the melt and affects the activity values, careful evaluation of oxygen solubility is essential. Also, suitable lead has to be chosen either for instant dipping or continuous immersion in the liquid alloy. Activities in Pb-Ni (116); Ni-Cr (123); Pb-Sn (46) systems have been determined by this technique.

### (ii) Oxides:

Only activity of PbO in liquid PbO-SiO<sub>2</sub> solutions (46, 111) has been determined by this method. Activity measurements are possible in various other liquid silicates and PbO-MO systems, but none have been reported so far probably due to the fact that the silicates and other liquid solutions of oxide are corrosive to the electrolytes employed presently.

#### D. Oxygen potentials in metal melts and gas mixtures:

Oxygen chemistry forms the basis of many industrially important metal extraction processes. Hence determination of oxygen contents and a knowledge of thermodynamics of oxygen in various metal melts is of considerable usefulness in exercising greater control over the metallurgical processes. In the conventional methods of analysis of oxygen, the metal melt has to be sampled and analysed physically or chemically for oxygen contents. In most of the cases, the methods are time-consuming, the results are postmortem in nature. In view of these difficulties, a probe device inserted directly into the molten melts which could give values of oxygen instantaneously would have obvious advantages. Electrochemical methods of measurement are attractive because they offer this possibility. By calibrating the emf of the cell



against the oxygen content measured by any one of the conventional methods, instantaneous determination of oxygen is possible. Also, the emf of the cell [7], gives directly the activity of oxygen in the melt. Knowing the solubility of oxygen, activity coefficient  $f_M^O$  in the melt can be determined. By studying the effects of various solutes on the activity of oxygen in metal melt, interaction coefficients  $e_M^O$  can be determined. Electro-chemical measurements of oxygen in liquid melts were reviewed by Littlewood (48), Fisher (137 e).

### D.1. Nonferrous melts:

Direct electrochemical determinations of oxygen and its activity in the liquid metals Ag (142 - 144), Sn (134), Pb (134), Cu (136, 137 a, 140-143), dilute Ag-Cu alloys (146) were reported. Coulometric titrations have been done (134) in liquid Sn and Pb by Bedford and Alcock to determine the standard free energies of solution of oxygen. Fisher et al (137 a) have determined standard free energies of solution of oxygen by measuring the cell emf and analyzing the melt for oxygen.

### D.2. Ferrous melts:

Instantaneous oxygen determination in steelmaking is of utmost importance in various refining and controlling operations. Analysis of various problems, methods of measurement are excellently dealt in papers by Fitterer et al (138); Baker & West (144); Fisher et al (137 a, 149); Fargeter (148); Fruehan & Turkdogan (151). The determination of oxygen using solid electrolytes have also been reported by various authors (129, 130, 133, 150). Oxygen probe consists of a disk of the electrolyte fused to one end of quartz tube with a reference electrode inside the probe. Emf readings stabilize within few seconds of immersion of the probe in the melt. It has been shown (138, 148, 151) that  $ZrO_2 - CaO$  functions adequately upto the oxygen contents corresponding to 10 PPM or more whereas  $ThO_2 - Y_2O_3$  electrolyte is applicable for oxygen levels of 1 PPM. The activities of oxygen have been measured (145) in Fe, Fe-Si, Mn and Fe-Mn melts. Effects of P, S, C, Co, Ni, Cr, V on the activities of

oxygen have been reported by Fisher et al (127).

### D.3. Partial Pressures of oxygen in gas mixtures:

By determining the  $p_{O_2}$  with the help of solid electrolyte cells,  $CO - CO_2$ ;  $C-CO-CO_2$ ; equilibrium has been studied by Peters & Moebius (127).  $H_2-H_2O$  equilibrium in the range 1550-1750°C was investigated by Fisher & Dieter (149). The importance of  $p_{O_2}$  measurement in various metallurgical industries was reviewed by Spacil & Schroder (55). Also  $p_{O_2}$  measurements using this technique have been reported by various authors (131, 132, 133, 139).

### E. Kinetic applications:

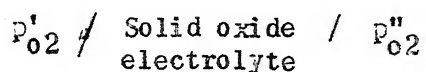
The possibilities of solid electrolytes for kinetic applications have been reviewed recently by Hickert (53, 153), Schmalzried (54) and D.C. Raleigh (51).

Rates of deoxidation of steels have been studied (152b, 155) by observing the changes in cell emf after the introduction of various deoxidizers in the steel melt. Mass transfer studies have been done by Nakelin & Bradshaw (154). They measured continuously the concentration of oxygen in a bath of liquid silver in which a jet of oxygen gas impinged. The uptake of oxygen was continuously noted by measuring the emf with a solid electrolyte tube. Also, the rates of oxidation and reduction of various oxides  $FeO$ ,  $Fe_2O_3$ ,  $Fe_3O_4$  (152a),  $NO_2$  (152c) could be determined with the help of suitable solid electrolyte cells. In all the kinetic studies,

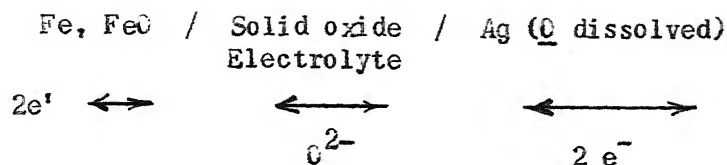
the reference electrode should be highly reversible for the proper interpretation of cell emfs. The polarization behaviour of the electrodes  $\text{Cu-Cu}_2\text{O}$ ;  $\text{FeO} - \text{Fe}_3\text{O}_4$  were studied by Iskoe & Morrell (161) to determine the limiting currents at which the electrodes are no more reversible.

The electrochemical methods using solid electrolytes have been used in a number of investigations of diffusivities of oxygen in various solid and liquid metals (156 - 160; 162 - 163). Most of the measurements were done on copper (158b, 160); Silver 156, 158b, 159) and lead (162, 163).

Consider the oxygen concentration cell



The open circuit emf gives the ratio of partial pressures of oxygen at the two electrodes. By applying a fixed potential to above cell, a predetermined ratio of oxygen partial pressures can be achieved. Thus, if  $p_{\text{O}_2}$  is fixed at one electrode and potential is applied to the cell, the other  $p_{\text{O}_2}$  is clearly fixed, provided the polarization is negligible. Kinetic applications are due to the fact that the flux of current through the above cell is a measure of the reaction rate by which oxygen is passed from one electrode to the other. In the determinations of oxygen diffusivities in metals, the metal is first brought into equilibrium with a fixed  $p_{\text{O}_2}$  in such a way that a known oxygen concentration is established in the metal. Then a galvanic cell is set up with a reversible metal-metal oxide electrode ( $\text{Fe-FeO}$ ) and the metal as the other electrode.



The above cell depicts the arrangement for diffusion measurement in silver by applying a potential such that oxygen concentration at the electrolyte-interface concentration is very much smaller than for Fe-FeO equilibrium, current passes through the cell in the indicated direction. This current is equivalent to oxygen diffusing out of the silver and from the knowledge of current density as function of time, and the initial oxygen concentration in silver, the diffusion coefficient of oxygen can be calculated. The method and analysis depends on the geometry employed for measurement. Linear geometry is useful for measurements in solid metals (156, 158a) whereas cylindrical geometry, in which a tube or crucible of solid electrolyte is made use of, is preferred for liquid metals (158b, 162, 163). In certain cases, the solubilities of oxygen in the solid metals can also be calculated (160).

#### F. Miscellaneous Applications:

Solid electrolytes have been used for analysis of nonferrous alloys (164), corrosion studies (166), and thermometry (165).

Wilder and Galin (164) have used the cell  $\text{Ni, NiO/ZrO}_2\text{-CaO/Zn}$  (in molten brass), ZnO to determine the zinc content in molten brass. In Cu-Zn-O system, the oxygen is present as ZnO and hence no ZnO has to be added separately in the right electrodes. By calibrating the emf of above



cell with zinc content in brass it has been conveniently used as an analytical tool. The error in analysis is claimed to be not more than 0.05 wt. %.

Galvanic cell of the type

Fe, FeO/Solid Oxide Electrolyte/Metal,

has been used by Mciver and Teale (166) to study corrosion of stainless Steels. The oxygen potential of slightly oxidised stainless steels at first approximates to the potential of Fe/FeO but after a short time the potential slowly decreases and becomes closer to underlying Cr/Cr<sub>2</sub>O<sub>3</sub> potential.

Solid electrolyte oxygen concentration cells have also been used by Lindsay and Ruka (165) to determine high fixed point temperatures such as melting point of Ag, In and Pd on the thermodynamic scale. They have analysed various sources of error and their results within a few degrees of the accepted values for In and Ag points.

#### G. Future Developments:

There is considerable scope for future thermodynamic investigations of solid and liquid solutions, molten silicates and various nonstoichiometric systems by solid electrolyte galvanic cells. Phase diagram studies involving solidus or liquidus determination in new alloy systems are likely to be extended. Activity determination as in alloy systems, comprising of metals closely resembling in their electronegativities will be possible, with increased thermodynamic knowledge of oxide systems. A definite knowledge of nonstoichiometry in metal oxides and oxygen solubility in liquid alloys

will be useful for further studies of liquid alloy systems using the solid electrolyte cell technique. Interaction coefficients of oxygen in alloy systems such as  $e_A^O$  (B),  $e_B^O$  (A) can be determined if dissociation and displacement reactions in dilute solutions are negligible.

Kinetic studies involving diffusion of oxygen in solid and liquid metals and alloys; vaporization and condensation phenomenon; phase boundary reactions; reduction and oxidation characteristics of various oxides, metals; mass transfer studies between liquid metals and gases; are likely to be pursued with much more vigour. With the development of suitable high temperature solid electrolyte, investigations of metallic systems at temperatures greater than  $1600^{\circ}\text{C}$  should be possible. Analytical studies such as oxygen determination in ferrous and nonferrous alloys, determination of the amount of reactive metal component in various liquid alloys will be pursued further. A variety of thermodynamic and kinetic studies will be possible with the development of new electrolyte systems, other than oxides, such as carbides, nitrides, sulphides and borides.

## CHAPTER III

PLAN OF THE WORKA. Previous work on copper-silver system:

Thermodynamic properties of liquid copper-silver alloys have been determined in the past by employing three methods, calorimetry (1, 6), vapor pressure measurement (3) and distribution equilibria (5). Phase diagram calculations have also been carried out (3).

Earliest calorimetric determinations of heats of formation of liquid copper-silver alloys for mole fraction of copper ( $X_{Cu}$ ) = 0.22 - 0.8, were done by Kawakami (1) in 1930. The more recent calorimetric measurements were done by Oriani and Murphy (6a) and Dakken and Elliott (6b). Oriani and Murphy investigated the compositional range  $X_{Cu} = 0.1$  to 0.8 at 1373°K, whereas Dakken and Elliott's investigations were confined to copper rich alloys,  $X_{Cu} = 0.6 - 0.9$  at 1373°K. Kawakami's measurements were found to be inaccurate and there is good agreement between the values of the latter investigators.

Edwards and Downing (3) measured the vapor pressures of silver and copper over liquid Cu-Ag alloys for  $X_{Cu} = 0.14 - 0.95$ , in the temperature range 1300-1560°K, by effusion cell technique. Activities were calculated at each temperature and the properties have been reported at the mean temperature of 1426°K. Eultgren (8) points out quite a few thermodynamic inconsistencies in Edwards and Downing's values. The activities of silver

show an increase in scatter as the mole fraction of silver ( $X_{Ag}$ ) goes up and at  $X_{Ag} = 0.56$ , the scatter is 10% of the mean value. Activity of silver ( $a_{Ag}$ ) does not merge into Raoult's law line when  $X_{Ag}$  tends to unity. Also the values of partial molar free energy of silver ( $F_{Ag}^M$ ) extrapolated to liquidus temperatures are found to be positive, when referred to solid silver as the standard state. Finally,  $F_{Cu}^K$  values derived from copper vapor pressures show a wide scatter.

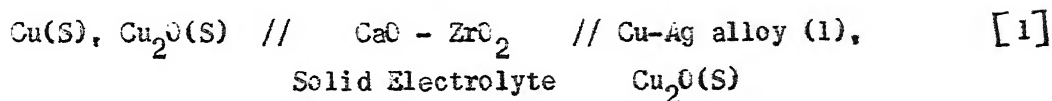
Koros and Chipman (5) measured activity of copper ( $a_{Cu}$ ) in liquid iron at 1873°K by equilibrating with Ag-Cu alloy. For this purpose they made phase diagram computations of  $\gamma_{Cu}$  in Ag using the measured heats of mixing of Kawakami at 1200°K. The terminal solid solutions are assumed to obey Raoult's law and the excess values of mixing of components in the liquid phase is obtained by an equation given by Wagner (13).

Kultgren et al (8) in their thermodynamic compilation, have critically reviewed these studies and reported the selected values for Ag-Cu system. They preferred the values of Oriani and Murphy for heats of mixing in liquid alloys. Assuming the thermodynamic properties of Cu-Fe system as correct, the selected values of  $F_{Cu}^M$  in the range  $X_{Cu} = 0.01-0.12$  were calculated from the measurements of Koros and Chipman. In the compositional range  $0.12 < X_{Cu} < 0.4$ ,  $F_{Cu}^M$  values were interpolated so that subsequent Gibbs-Duhem integration would yield a value of  $F_{Ag}^M$  at the eutectic point which was consistent with the properties of solid phases. The selected properties of liquid alloys in this range are not consistent with the properties of  $\mathcal{L}$  phase, liquidus and solidus temperature.

Hence more accurate determinations on the thermodynamics of liquid alloys and phase diagram, are needed in this range.

### B. Plan of the present work:

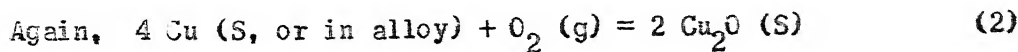
The preceding discussions clearly point out the need for more precise determinations in the liquid Cu-Ag alloys. Therefore, direct measurements of activity were planned in this system by solid electrolyte galvanic cell method. Various investigators have demonstrated ~~emf~~ measurements with the solid oxide electrolyte are capable of yielding results with good accuracy. In the present work, the cell was



This type of cell has been employed by Cavanaugh and Elliott (116) and Goto and St. Pierre (126) for activity determinations in liquid alloys, and is of the general type A, AO // Solid oxide // A-B alloy, AO [2]  
Electrolyte

Such cells yield activity values of A in the alloy A-B directly from the cell emf's. In cell, if  $p_{\text{O}_2}^{\text{o}}$  and  $p_{\text{O}_2}$  are the partial pressures of oxygen in equilibrium with Cu and  $\text{Cu}_2\text{O}$ , on the left and right sides of the electrolyte, then

$$E = \text{Emf of the cell} = \frac{R}{4F} T \ln \frac{p_{\text{O}_2}^{\text{o}}}{p_{\text{O}_2}} \quad (1)$$



$$K = a_{\text{Cu}_2\text{O}}^2 / (a_{\text{Cu}}^4 \times p_{\text{O}_2}) \quad (3)$$

If  $\text{Cu}_2\text{O}$  is pure, 
$$p_{\text{O}_2} = \frac{1}{K \cdot a_{\text{Cu}}^4} \quad (4)$$

Taking the pure solid copper as the standard state and combining equations, we obtain

$$E = - \frac{RT}{F} \ln a_{\text{Cu}} \quad (5)$$

or 
$$F_{\text{Cu}}^M = - EF \quad \& \quad S_{\text{Cu}}^M = - \frac{F_{\text{Cu}}^M}{dT} = F \left( - \frac{dE}{dT} \right) \quad (6)$$

Gibbs-Duhem integration can yield partial thermodynamic properties of silver. From these partial values, integral and excess values can be calculated in the usual manner.

To employ solid electrolyte cell technique, the requirements enlisted in Ch. II, have to be satisfied. The calcia-stabilized zirconia is a perfect ionic conductor (47) in the range of  $p_{\text{O}_2}$  prevailing during the experimental conditions ( $p_{\text{O}_2} > 10^{-10}$  atoms).  $\text{Cu}_2\text{O}$  is much more stable than  $\text{Ag}_2\text{O}$  and hence  $p_{\text{O}_2}$  at each electrode is dictated by Cu (S or in alloy) -  $\text{Cu}_2\text{O}$  equilibrium alone. The difference of standard free energies of formation ( $\Delta F^\circ$ ) of  $\text{Ag}_2\text{O}$  and  $\text{Cu}_2\text{O}$  is of the order of 60,000 cal. Therefore, the formation of  $\text{Ag}_2\text{O}$  in the melt is not possible and the displacement reaction  $\text{Cu}_2\text{O} + 2\text{Ag} = 2\text{Cu} + \text{Ag}_2\text{O}$  cannot take place.  $\text{Cu}_2\text{O}$  exhibits little non-stoichiometry in the experimental temperature range of 780-1050°C. This is evident from the Cu-O phase diagram given in Hansen (4). Above 1230°C,  $\text{Cu}_2\text{O}$  decomposes into Cu<sub>2</sub>O and O<sub>2</sub>. Upto approximately 1065°C,

almost pure solid copper will be in equilibrium with solid  $\text{Cu}_2\text{O}$ . Above  $1065^\circ\text{C}$ ,  $\text{Cu}_2\text{O}$  will be no longer in equilibrium with pure copper but with liquid Cu and a few percentage of oxygen dissolved. Hence the upper temperature limit for the successful operation of the cell would be  $1060^\circ\text{C}$ . Thus, a temperature range of 100 to  $250^\circ\text{C}$  is possible in this investigation. Except in predominantly copper-rich or silver-rich alloys, the temperature coefficients of the cell would be fairly reliable and thermodynamic properties of liquid copper-silver alloys can be found out. Oxygen solubilities in pure Cu and Cu-Ag alloys to be investigated must be as small as possible. Otherwise the system under study would be a ternary system Cu-Ag-O and the oxygen may have strong influence on the activity values of copper. Below  $1050^\circ\text{C}$ , there is negligible solubility of oxygen in solid copper. Since oxygen solubility data on Ag-Cu alloys is lacking, preliminary estimate was made from Tankin & Belton's (22) model. This model permits the estimation of solubilities in binary metallic alloys from the energies of solution of oxygen in the component metals. Calculations based on this model revealed that solubility is nearly 1 atom percent for  $X_{\text{Cu}} = 0.15$ . Thus Cu-Ag system satisfies most of the requirements for the solid electrolyte galvanic cell measurements.

The work was planned in three parts.

(i) Calibration run: A galvanic cell with known ~~emf~~ and the

$\text{Cu}, \text{Cu}_2\text{O} // \text{Solid Electrolyte} // \text{Ni}, \text{NiO}$

[3]

measured emf can be compared with precise values of this cells that are available in literature. Good match between the observed and actual values would establish the soundness of the electrolyte and the cell geometry employed i.e. absence of electronic conductivity in the electrolyte, negligible gas transport between the two electrode compartments.

(ii) Selection of lead for the liquid alloys: Dissolution of the lead in the liquid alloy is a serious problem in this kind of studies. Hence trial runs using various leads have to be taken to establish the right kind of lead to be employed for immersion in liquid Cu-Ag alloys. Ta, Mo, inconel,  $\text{Cu}_2\text{O}$  coated Cu,  $\text{Cu}_2\text{O}$  and cermets were possible choices of lead wires.

(iii) Experiments on copper-silver system: Taking all the preceding considerations into account, it was decided to investigate the compositional range,  $X_{\text{Cu}} = 0.1$  to  $0.9$  between  $1050^\circ\text{C}$  and liquidus temperature of the alloy.



## CHAPTER IV

APPARATUS AND EXPERIMENTAL TECHNIQUESA. Furnace and Reaction Tube:

The furnace used was a vertical globar furnace in which the six globars equally spaced from the center served as heating elements. The furnace was designed to operate upto a maximum temperature of  $1400^{\circ}\text{C}$ . After the furnace was set in operation, temperature profile was taken and length of constant temperature zone was found to be at least  $1\frac{1}{2}$ ". Power to the furnace was supplied from a voltage stabilizer, connected straight to the mains.

The reaction tube was of mullite (O.D  $2\frac{3}{4}$ ", I.D  $2\frac{1}{2}$ ", Ht. 20"), fitted with two brass heads at either end Brass heads contained grooves in which silicone rubber gaskets could be tightly fitted. Brass heads could be rigidly clamped to the reaction tube, the ends of which pressed against the groove and made it gas tight. Bottom brass head was sealed permanently with white RTV silicone sealant. Purified argon could be introduced into the furnace through a port in the bottom brass head. Top brass head had individual ports for thermocouple sheaths, lead wires, addition tube and argon outlet tube. Stainless tubes brazed to the brass head acted as guide tubes. Around the periphery of top brass head, a single round of copper tubing was soldered to it and water could be continuously circulated through the tubing to keep the head cool. A peep hole covered with blue glass was

provided in the brass head to assist in viewing the cell assembly.

B. Temperature Control and Measurement:

The temperature of the furnace could be controlled within  $\pm 1^\circ\text{C}$  using electromax signalling controller coupled to a relay mechanism and a chromel-alumel thermocouple. The thermocouple with a double bore alumina sheath was placed right in the center of the furnace through a hole drilled across the furnace shell. The temperature of the inside cell assembly was independently measured by a calibrated platinum-platinum/10% rhodium thermocouple using Leeds and Northrup potentiometer - model 8686.

C. Emf Measurement:

A potentiometer assembled in the laboratory was used for emf measurements.

Specifications: Galvanometer-2435 series, Reflection type sensitivity - 0.025 microamperes per scale division, Potentiometer - model 7645

Galvanometer and Potentiometer were Leeds and Northrup make.

D. Gas Train:

Argon was purified by successively passing it through a copper-gauge furnace maintained at  $550^\circ\text{C}$ , series of  $\text{CaCl}_2$  and  $\text{P}_2\text{O}_5$  towers and finally through magnesium-chip furnace at  $500^\circ\text{C}$ . Copper gauge and magnesium chip furnaces were of resistance wound type and were designed

in the laboratory. Copper and magnesium act as oxygen getters while  $\text{CaCl}_2$  and  $\text{P}_2\text{O}_5$  absorb the traces of moisture in argon. During the experiments, stream of purified argon at slow flow rate was maintained in the furnace chamber. Slight positive pressure was maintained inside the furnace. The flow rate could be visually inspected as argon flows through the bubblers at the inlet and outlet ends.

#### E. Experimental Materials:

Following materials were used in the cell set up.

1. Solid electrolyte crucible -  $\frac{3}{8}$ " I.D,  $\frac{1}{2}$ " O.D, 1" high 15 mole percent calcia-stabilized zirconia. Supplied by Zirconium Corporation of America.
2. **ZIRCOA** - B powder - Zirconia fully stabilized with calcia(- 325 mesh)
3. Nickel and copper - Semi elements inc. U.S.A., Purity greater than 99.97%
4. Silver - American Smelting and Refining Co., U.S.A.; Purity 99.99%
5. Platinum and Pt-10% Rh - Baker Co., U.S.A., Thermocouple and commercial grade
6. Cuprous oxide and Nickel oxide - Fisher certified reagents
7. Metamic 612 cermets - Approximately contains 72% Cr, 20%  $\text{Al}_2\text{O}_3$ , rest silica and other constituents; Morganite Ltd.,
8. RTV silicon sealant - white (Pourable) GEC.

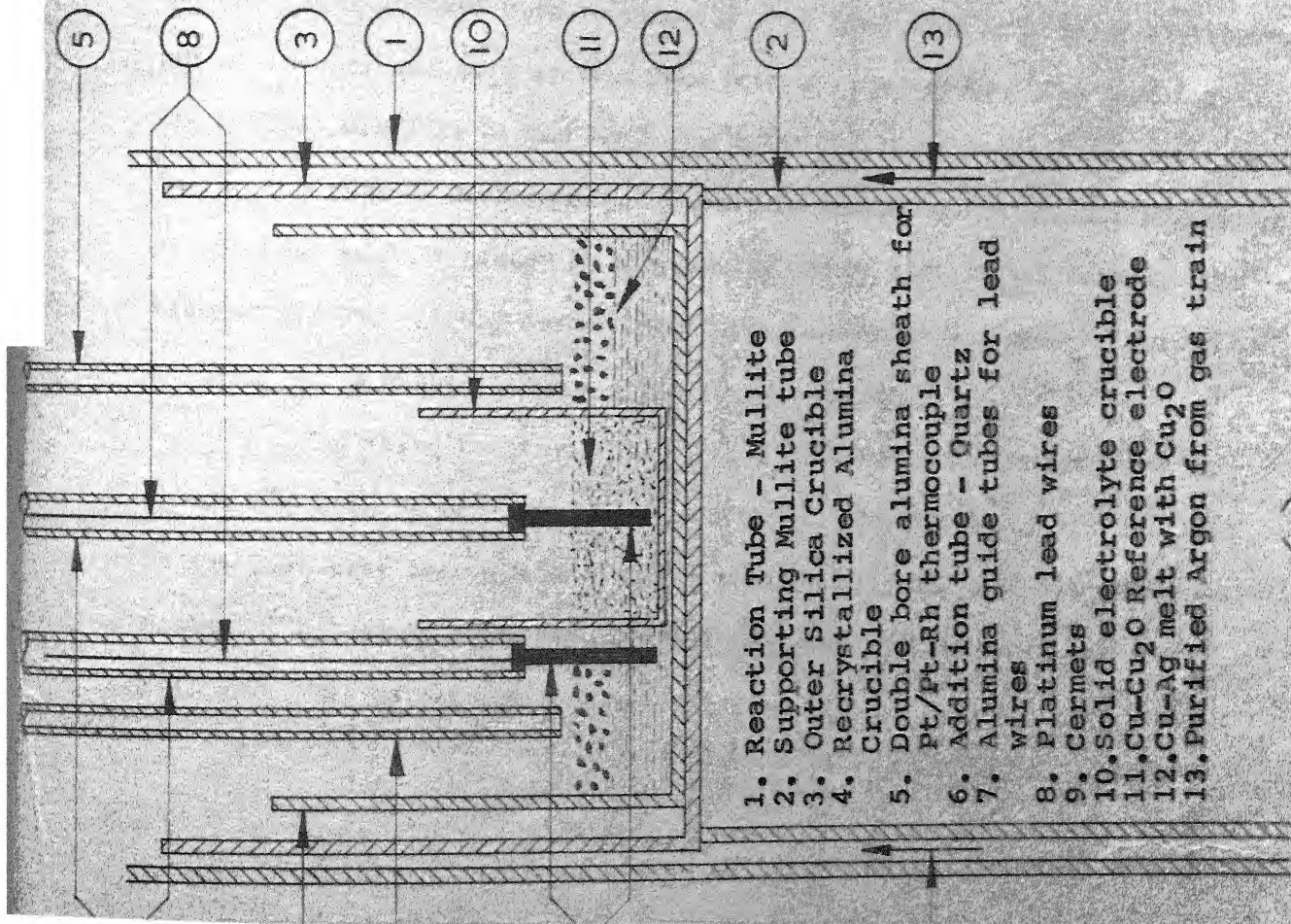
### F. Cell Assembly:

The cell consists of solid electrolyte in contact with two electrodes on either side of it. Two types of cells as shown schematically in Fig. 1a and b were employed in the present work.

In cell a, the electrolyte was 15 mol % Calcia stabilized zirconia crucible and the reference electrode was finely ground mixture of copper and cuprous oxide. The electrolyte crucible served as the container. recrystallized alumina crucible or a laboratory made zirconia crucible was used as the container for the test electrode Cu-Ag alloy and  $\text{Cu}_2\text{O}$ .

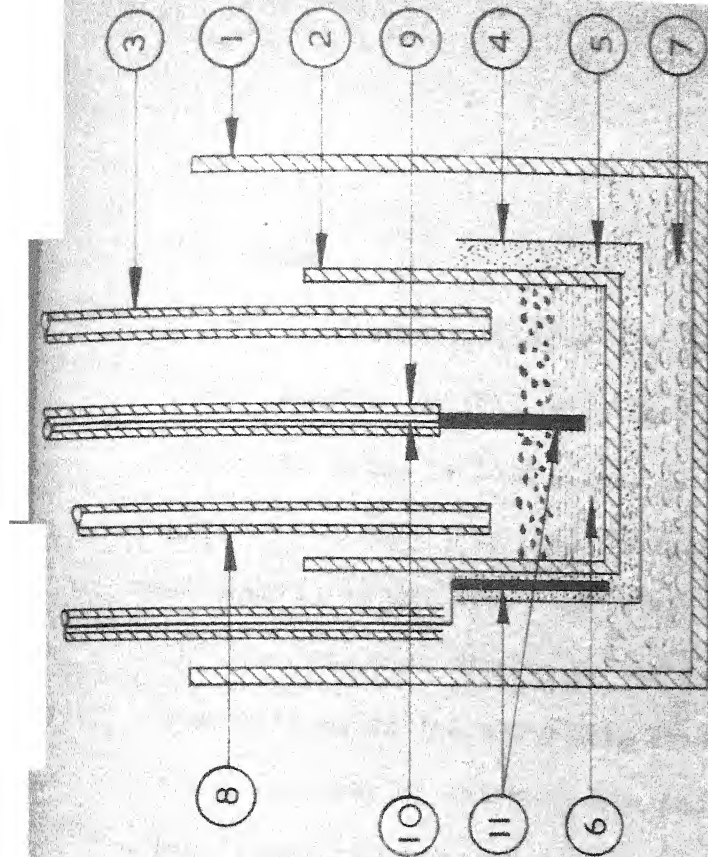
In cell b, laboratory made crucibles from fully stabilized ZIRCOA-B powder, served as the electrolyte. The crucibles were slip-cast, presintered at  $1200^\circ\text{C}$  for one day and finally sintered at  $2000^\circ\text{C}$  for 6 hrs. in ZIRCOA pot furnace. Further details of crucible preparation are given in Appendix - C. Thin copper foil was wrapped around the electrolyte crucible and the annular gap was filled with Cu- $\text{Cu}_2\text{O}$  mixture. The test electrode of Cu-Ag alloy with  $\text{Cu}_2\text{O}$  was placed inside the electrolyte crucible. The electrolyte crucible was placed inside a recrystallized alumina or another zirconia crucible with Cu shots along with  $\text{Cu}_2\text{O}$  is placed in the outer crucible to promote local equilibrium.

The whole cell assembly was placed in a silica crucible (O.D  $1\frac{7}{8}$ , 4" height), resting on the supporting mullite tube. It was ensured that cell assembly was in the constant temperature zone.



1. Reaction Tube - Mullite
2. Supporting Mullite tube
3. Outer Silica Crucible
4. Recrystallized Alumina Crucible
5. Double bore alumina sheath for Pt/Pt-Rh thermocouple
6. Addition tube - Quartz
7. Alumina guide tubes for lead wires
8. Platinum lead wires
9. Cermet
10. Solid electrolyte crucible
11. Cu-Cu<sub>2</sub>O Reference electrode
12. Cu-Ag melt with Cu<sub>2</sub>O
13. Purified Argon from gas train

(a) x



1. Recrystallized alumina crucible
2. Solid electrolyte crucible
3. Quartz tube for addition
4. Thin copper foil
5. Cu-Cu<sub>2</sub>O reference electrode
6. Cu-Ag melt with Cu<sub>2</sub>O
7. Cu shots with Cu<sub>2</sub>O
8. Double bore Alumina sheath
9. Alumina guide tubes for lead wires
10. Platinum lead wires
11. Cermet

(b)

### G. Leads:

Considerations of the lead for liquid alloy were already discussed under Ch. II. In this study Cu coated with  $\text{Cu}_2\text{O}$ , Inconel, cermet and sintered  $\text{Cu}_2\text{O}$  were tried as lead wires. Cu was partly oxidized to  $\text{Cu}_2\text{O}$  and trials carried out with this lead revealed that there was considerable dissolution of underlying Cu, even with instant dipping. Next, inconel was tried and in this case also dipping of the lead in the alloy was momentary. Two compositions of the alloy were studied using inconel as lead. Except for the difficulty of lowering down the lead into the melt, everytime a measurement was taken, inconel seemed to be a satisfactory lead wire. Though an oxide coating was observed on inconel, it did not affect the results. The emf's measured with inconel were reproducible and reversible. To eliminate thermal emf's, inconel was used as lead for both the electrodes. The lead for Cu-Ag alloy was just placed above the melt when measurements were not taken. During the time of measurement, it could be pushed easily due to the elasticity of silicone scalant placed in the annular gap of the inconel lead and the alumina sheath. It was observed that inconel could be dipped in the melt at least for a minute without affecting the results.

The third trial was done with a chromium based cermet, similar to the one used by Diaz and Richardson(143). Advantages of cermet lie in the fact that they can be immersed continuously and make the experimentation easier. The cermet got superficially oxidized but this did not affect the cell emf. The potentials measured with the help of cermet proved to be quite

reversible. In view of the large oxygen potential difference between  $\text{Cr}_2\text{O}_3$  and  $\text{Cu}_2\text{O}$ , negligible amount of chromium from the cermet is expected to dissolve. Diaz and Richardson's (143) analysis of copper-oxygen melts in contact with the cermet for 10 days at  $1100^\circ\text{C}$  revealed that .02% Cr has dissolved. The cermets were hung by platinum wires and they were kept in position by tying them to the alumina guide tubes or closely fitting them in the alumina tube, as shown in Fig. 1. Most of the runs were taken with the cermets.

Sintered cuprous oxide ( $\text{Cu}_2\text{O}$ ) in the form of thin rod was also tried as lead. Fine  $\text{Cu}_2\text{O}$  powder was packed tightly in one end closed quartz tube and a platinum wire was placed in the powder.  $\text{Cu}_2\text{O}$  was isintered on to the platinum wire by heating the quartz tube to  $1000^\circ\text{C}$  for about 10 hrs under argon atmosphere. Quartz tube was gently broken so as to cause little damage to the sintered rod. The positioning of this lead in the cell was similar to that of cermet and gave reproducible and stable values of emf's.

#### H. Calibration runs:

The cell a was used in most of the runs. In order to make sure that there was no significant gaseous transport via atmosphere and electronic conductivity in the electrolyte, a calibration run was taken with mixtures of Cu-Cu<sub>2</sub>O and Ni-NiO as the two electrodes.

The electrode mixtures were prepared by thoroughly grinding the metal-metal oxide powders in an agate mortar. Cu-Cu<sub>2</sub>O mixture was packed inside the electrolyte crucible upto half of its height. The contact to



this reference electrode was established by pressing a platinum disk, which was spot-welded to Pt and Pt/10% Rh wires, sheathed in a double bore alumina tube. This served as lead as well as thermocouple. Platinum wire was wound round the electrolyte crucible and a moist paste of Ni-NiO was applied over it. This platinum wire was sheathed in a single bore alumina tube and served as the lead from the test electrode. The electrolyte crucible was placed inside a recrystallized alumina crucible containing Ni-NiO mixture so as to promote local thermodynamic equilibrium. The alumina sheaths carrying lead wire and thermocouple wires were brought out of the furnace by passing them through the stainless tubes of brass head and it was tightly clamped to the reaction tube. All the openings in the brass head were closed using the scalant and the furnace chamber was made gas tight.

The furnace chamber was first flushed with purified argon and then slowly heated to  $200^{\circ}\text{C}$ . The temperature was maintained at  $200^{\circ}\text{C}$  for about 2 hrs and the moisture from the moist paste of Ni-NiO was evacuated and flushed out with argon repeatedly. Then the furnace was slowly heated to  $900^{\circ}\text{C}$  in about 8 hrs under a slow flow of purified argon. Both the electrode mixtures got sintered 'insitu' establishing very good electrical contact. The duration of the run was about one week and the temperature cycling was done two times in the range 750 to  $1050^{\circ}\text{C}$ . Below 750 and above 1050 the cell emf's were not reproducible. The cell was allowed to equilibrate at the desired temperature and the measured emf was considered as equilibrium one, if it remained constant within  $\pm 0.2$  mV for a minimum period of 6 hrs.



Usually the temperature setting was left unchanged for at least 8 hours. Also, the cell was left overnight and at times for one full day at arbitrarily selected temperatures. The emf's remained steady and the fluctuations were always within 0.5 mV. Only during the end of the run (on 8th day), cell deteriorated and the run was abandoned. During the emf measurements, reversibility tests were administered. Flow rates were varied between 15 bubbles per min. to 150 b/m at least twice a day. No adverse effect was noticed on the cell and the emf remained steady ( $\pm 0.2$ ). The reversibility was also tested by imposing emf on the cell from an external source in either direction, and observing the behaviour of the system. The emf approached equilibrium value within half an hour of the polarization and took maximum of two hours to become steady. The calibration run results are presented in the Appendix-A and these values are compared with the precise values available in the literature in Table I and the agreement was excellent.

The cell b was calibrated against cell a by measuring the emf vs. temperature relation for the same alloy ( $X_{\text{Cu}}=0.5$ ) in both the cases. The emf's from a & b cells matched within 1 mV and hence it was concluded that cell b. was also good for measurements on liquid alloys.

#### I. Experiments on Cu-Ag system:-

The master alloys of copper and silver were prepared by melting the required amounts of these metal shots either in evacuated and sealed quartz tubes or in one end open quartz tube under a stream of purified argon.

Weight of each master alloy ranged between 7 and 10 grams. The alloys were taken in the recrystallized alumina crucible (cell a) or in the electrolyte crucible (cell b) along with 1 to 2 gms. of  $\text{Cu}_2\text{O}$ . The whole cell assembly with the leads in position was encased in the silica crucible and was lowered into the furnace.

After making the furnace chamber gas tight, it was flushed with argon and evacuated around  $150^\circ\text{C}$  with the cell assembly in position. It was filled with argon and then slowly heated to  $1000^\circ\text{C}$  in about 9 hrs. At this temperature, the cell used to attain equilibrium in less than two hrs. Emf's were recorded at intervals of 30 minutes and if the variation was within  $\pm 0.1$  mV in a period of 2 hrs, the values were considered to be equilibrium ones. <sup>6</sup> Almost instantaneous response was noticed in the all emf's whenever temperature changes were effected. In all the runs, the stability of emf with time was tested by leaving the cell undisturbed for at least 6 hrs. The variations in emf never exceeded 0.5 mV. Changes in gas flow rates did not affect the results. The reversibility of the cell used to be checked by polarizing it in both directions. Even after heavy polarization (1 mV for 3 mts.), emf's approached the equilibrium value within 5 mts. and usually a maximum of 30 minutes were enough for attainment of steady emf's.

In the same run, more than one composition could be studied by appropriation additions of the metal shots through the quartz addition tube filled with a removable cap at the top. It was held  $\frac{1}{2}$ " above the melt by

sealing it to the stainless steel tube with the silicon sealant. Addition time was kept to minimum and during this period high flow rate of argon was maintained to avoid any possible oxidation of the alloy. Immediate changes in emf's upon addition were observed and steady emf's used to be attained in about 2 hours time.

Chemical analysis of the alloys were not done. In order to make sure of the constancy of the compositions during the runs, a few times the same compositions were obtained either directly from master alloys or additions. Emf's by these two procedures differed by less than 1 mV. This observation coupled with the fact that, the temperature cycling yielded reproducible emf's and the emf vs. temperature plots were essentially linear with standard deviations of less than 1 mV in all the runs, pointed out to the negligible compositional changes during the runs either through evaporation of silver or in any other possible manner.

## CHAPTER V

RESULTS and DISCUSSIONS

## A. Results:

The measurements were mainly confined in the range of  $X_{\text{Cu}}=0.1-0.6$  and in the temperature  $T$  liquidus to  $1330^{\circ}\text{K}$ . A few measurements were done below the liquidus temperature and above  $1330^{\circ}\text{K}$ . Though the compositions  $X_{\text{Cu}} = 0.25$  and  $0.9$  were studied, it was felt that the measurements were not precise enough to derive the various thermodynamic properties and hence they were not considered. Nevertheless, cell emf as a function of temperature for all the compositions investigated are given in the Appendix-A.

A computer programme was developed to derive partial molar values of copper from the basic emf data of the cell. This programme can be modified to derive all the thermodynamic properties of alloys in certain limiting cases. Firstly, least square linear relationships were fitted between emf and temperature, then, activities ( $a_{\text{Cu}}$ ); activity coefficients ( $\gamma_{\text{Cu}}$ ); partial molar values of free energy, entropy and enthalpies of mixing ( $F_{\text{Cu}}^{\text{M}}$ ,  $S_{\text{Cu}}^{\text{M}}$ ,  $H_{\text{Cu}}^{\text{M}}$ ); Alpha functions ( $\alpha_{\text{Cu}}$ ) and Beta functions ( $\beta_{\text{Cu}}$ ) of copper were calculated from the cell data. The program used is presented in the Appendix-B.

The cell emfs give partial quantities for copper directly with solid copper as the standard state. For interpretation of thermodynamic properties of liquid alloys, standard state of pure liquid metal is preferable. Hence, the liquid copper was employed as the standard state by

making appropriate corrections for fusion values of copper. The partial quantities of copper are calculated using the following equations,

$$F_{\text{Cu}}^M = - \Delta F + \Delta F_{\text{fusion}} = RT \ln a_{\text{Cu}} \quad (1)$$

$$S_{\text{Cu}}^M = F \frac{dF}{dT} - \Delta S_{\text{fusion}} \quad (2)$$

$$H_{\text{Cu}}^M = F_{\text{Cu}}^M + T S_{\text{Cu}}^M \quad (3)$$

In the experimental range of temperature,  $H_{\text{Cu}}^M$  and  $S_{\text{Cu}}^M$  are considered as constant. The partial thermodynamic quantities for silver can be determined, with liquid copper as the standard state using the following equations

$$\log a_{\text{Ag}} = \log X_{\text{Ag}} - X_{\text{Ag}} X_{\text{Cu}} \mathcal{L}_{\text{Cu}} + \int_0^{X_{\text{Cu}}} \mathcal{L}_{\text{Cu}} \cdot dX_{\text{Cu}} \quad (4)$$

$$F_{\text{Ag}}^M = 4.576 T \log a_{\text{Ag}} \quad (5)$$

$$H_{\text{Ag}}^M = - X_{\text{Ag}} X_{\text{Cu}} \beta_{\text{Cu}} + \int_0^{X_{\text{Cu}}} \beta_{\text{Cu}} \cdot dX_{\text{Cu}} \quad (6)$$

$$S_{\text{Ag}}^M = (H_{\text{Ag}}^M - F_{\text{Ag}}^M) / T \quad (7)$$

where,

$$\mathcal{L}_{\text{Cu}} = \log \gamma_{\text{Cu}} / (1 - X_{\text{Cu}})^2 \quad (8)$$

$$\beta_{\text{Cu}} = H_{\text{Cu}}^M / (1 - X_{\text{Cu}})^2 \quad (9)$$

The integrals in the equations (4) and (6) have been evaluated graphically from Figs. 4 and 5. From these partial values, integral and excess

molar properties of mixing are calculated as follows.

$$F^M = X_{Cu} F_{Cu}^M + X_{Ag} F_{Ag}^M \quad (10)$$

$$H^M = H^E = (1 - X_{Cu}) \int_0^{X_{Cu}} \beta_{Cu} \cdot dX_{Cu} \quad (11)$$

$$S^M = (H^M - F^M)/T \quad (12)$$

where  $F^M$ ,  $H^M$ ,  $S^M$  are integral molar free energy, enthalpy and entropies respectively.  $F^E$ ,  $S^E$  are excess molar properties and can be evaluated using

$$F^E = (1 - X_{Cu}) \int_0^{X_{Cu}} \alpha_{Cu} \cdot dX_{Cu} \quad (13)$$

$$S^E = (H^M - F^E)/T \quad (14)$$

## B. DISCUSSION:

Emf versus temperature plots for  $X_{Cu} = 0.1$  to  $0.6$  are shown in Fig. 2. Table II presents the results analytically, along with the standard and maximum deviations. Details of cell and leads employed are clearly depicted in Fig. 2. The emfs have been extrapolated to  $1400^\circ\text{K}$ , after correcting for  $\frac{dE}{dT}$  at the melting point of copper ( $1356^\circ\text{K}$ ). Since the range of extrapolation is small (about  $70^\circ$ ), the extrapolation is justified. The extrapolated values at  $1400^\circ\text{K}$  are useful in comparing the values of this work with the selected values reported by Muttgren et al (6). The cell data are independent of the geometry and the leads employed. They

were unaffected by the changes in gas flow rates and polarization tests showed excellent reversibility. Stray emfs were not encountered, since the same emfs were obtained irrespective of whether the furnace supply was on or off. Emfs were measured below liquidus for a few compositions only. Hultgren et al (8) give a value of  $0.96 \pm .005$  for the activity of copper at the eutectic temperature ( $1052^{\circ}\text{K}$ ). The emf data at the eutectic composition  $X_{\text{Cu}} = 0.4$  and  $X_{\text{Cu}} = 0.7$  yielded values of 0.953 and 0.965 respectively. This agreement is considered quite good. The emf for  $X_{\text{Cu}} = 0.7$  near the eutectic temperature is not shown in Fig. 2 but the value is reported in Appendix - A. At  $X_{\text{Cu}} = 0.1$ , the liquidus determined is  $13^{\circ}\text{C}$  higher than that interpolated from the phase diagram. Repetition with another master alloy of same composition, yielded reproducible results. At  $X_{\text{Cu}} = 0.2$  and 0.3, considerable supercooling (greater than  $20^{\circ}\text{K}$ ) was observed. Even prolonged equilibration (12 to 18 hours) and stirring of the bath resulted in the same emfs. The dissolved oxygen could be the cause for the lowering of liquidus at  $X_{\text{Cu}} = 0.2$  and 0.3. But the higher liquidus at  $X_{\text{Cu}} = 0.1$  can not be explained in the absence of chemical analysis of the alloy for oxygen and copper contents of the alloy.

The activities of copper and silver at  $1200^{\circ}$ ,  $1300^{\circ}$ ,  $1400^{\circ}\text{K}$  (extrapolated) are presented in Fig. 3 and Table III along with the values reported by Hultgren et al (8). The standard states for both are pure liquid metals. For determination of activity of silver, extrapolated value of  $a_{\text{Cu}}$  was employed only for  $X_{\text{Cu}} = 0.8$ , since at this composition

$\gamma_{\text{Cu}}$  is close to unity and a little error in  $a_{\text{Cu}}$  can lead to a large uncertainty in  $\mathcal{L}_{\text{Cu}}$ . The extrapolated values at 1400°K are 10 to 15% higher on silver rich side and 3 to 5% lower on high copper side, compared to those of Hultgren et al (8).

As Table IV shows  $H_{\text{Cu}}^{\text{M}}$  obtained from the intercepts of emf versus temperature plots increase with decreasing  $X_{\text{Cu}}$ , except at  $X_{\text{Cu}} = 0.1$ , where it is unusually low. The large change in solubility of oxygen with temperature could be causing the discrepancy. Quantitative explanation could not be given in the absence of oxygen solubility data in these alloys. If  $\text{Cu}_2\text{O}$  will dissolve in the liquid alloy according to the reaction,



it can lead to an increase in  $X_{\text{Cu}}$  by fraction of few hundredths, which is enough to decrease the slope of emf versus temperature plot and hence decrease measured  $H^{\text{M}}$  considerably. This process is reversible with temperature and hence temperature cycling will not reveal any irreproducibility.

Approximate calculations on the basis of model proposed by Belton and Tankins (22) for the solubility of oxygen in binary alloys, confirms that oxygen solubility is nearly 1 atom % at 1300°K for silver rich alloys ( $X_{\text{Cu}} = 0.15$ ). The detailed procedure of estimation is shown in the Appendix - D. Using the standard free energies of solution oxygen in copper and silver and the equilibrium  $p_{\text{O}_2}$  over Cu-Ag alloys with  $\text{Cu}_2\text{O}$ , the solubility of oxygen in the alloys can be calculated. These calculations are qualitative in nature and hence serious deductions cannot be made unless precise oxygen solubilities



and its effect on the activity of oxygen are known. The inaccuracy in the activity of copper at  $X_{\text{Cu}} = 0.1$ , from the slope changes of  $E_{\text{mf}}$  - temperature plots, due to changes in oxygen solubility is estimated to be not more than 3% at 1300°K. For  $X_{\text{Cu}} = 0.2$ , the dissociation of  $\text{Cu}_2\text{O}$  will not cause appreciable compositional changes (less than .005 in  $X_{\text{Cu}}$ ). Moreover, the emf values for the alloys are much less sensitive to slight compositional changes and the resulting changes in  $H_{\text{Cu}}^{\text{M}}$  will be well within the experimental uncertainty. Even if an approximate correction for oxygen solubility, could be made in  $a_{\text{Cu}}$  values for  $X_{\text{Cu}} < 0.4$ , our values seem to be higher than the values reported by Hultgren et al (8). Integral and excess molar free energies of mixing ( $F^{\text{M}}$  and  $F^{\text{E}}$ ) of this work are compared with those of Hultgren et al (8) in Fig. 6 and the agreement is quite good.

Extrapolated values of  $\beta_{\text{Cu}}$  were preferred at  $X_{\text{Cu}} = 0.1$  and 0.8. At  $X_{\text{Cu}} = 0.8$ ,  $\beta_{\text{Cu}}$  is very much sensitive and an uncertainty of .005 in the temperature coefficient of the cell emf will lead to a large error in  $H_{\text{Cu}}^{\text{M}}$  and  $\beta_{\text{Cu}}$ . As Fig. 7 shows, our values for integral molar heats of mixing  $H^{\text{M}}$  agree well with calorimetric values (1, 6) in the high Cu range, whereas in the lower copper side, our values are somewhat lower. Considering the uncertainty of nearly 200 cal in  $H^{\text{M}}$  values of present work, the agreement is good.

Uncertainty analysis of the various thermodynamic quantities were performed for a typical composition  $X_{\text{Cu}} = 0.5$  at 1300°K. The various uncertainties are shown in brackets in Table IV. The detailed procedure of uncertainty estimates is given in Appendix - E.

## CHAPTER VI

SUMMARY and CONCLUSIONS

Liquid copper-silver alloys were investigated using solid electrolyte cell technique. From the basic cell emf data, various thermodynamic functions of liquid copper-silver alloys for  $X_{\text{Cu}} = 0.1 - 0.8$  were determined and reported at a temperature of  $1300^{\circ}\text{K}$ . The thermodynamic values of this work extrapolated to  $1400^{\circ}\text{K}$  were compared with the selected values of Hultgren et al (8). The activity data obtained from this work are considered to be more accurate than the previous data. The calculated integral heats of mixing from the emf and the temperature coefficient of the cell, agree with the recent accurate calorimetric determinations within the experimental uncertainty. At few compositions, graphically extrapolated values of Alpha and Beta functions were preferred rather than the experimental values, as these are subjected to serious errors despite small uncertainties in cell emf data. The liquidus temperatures determined for few compositions of silver-rich alloys do not match with those of phase diagram. The oxygen solubility in copper-silver alloys is thought to be one of the main reasons for the above discrepancy. For accurate estimation of entropies of mixing, the accurate activity values of this work should be combined with the precise heats of mixing values from calorimetric work.

## CHAPTER VII

SUGGESTIONS FOR FURTHER WORK

Further work on Cu-Ag system consists in accurate determination of liquidus temperatures and the effect of oxygen solubilities on the liquidus solid Cu-Ag alloys can also be investigated by this technique to establish the solidus of the system accurately. If the oxygen solubilities are compatible with the solid electrolyte cell requirements, activities in binary Cu-Au and ternary Cu-Ag-Au systems can be investigated. Activity of oxygen in dilute Cu - X - O systems can be determined by emf method to understand the thermodynamics of oxygen in dilute solutions and for model studies in these solutions. Coulometric titrations are convenient means for the determination of activity coefficients and interaction coefficients and can be used to determine these thermodynamic quantities in Cu - X - O solutions. Also, activity calculations of  $\text{Cu}_2\text{O}$  can be made in  $\text{Cu}_2\text{O}$  - XO systems such as  $\text{Cu}_2\text{O}$  -  $\text{PbO}$  by emf technique. Kinetic studies such as oxygen diffusivity determinations in Cu - X solutions are possible.

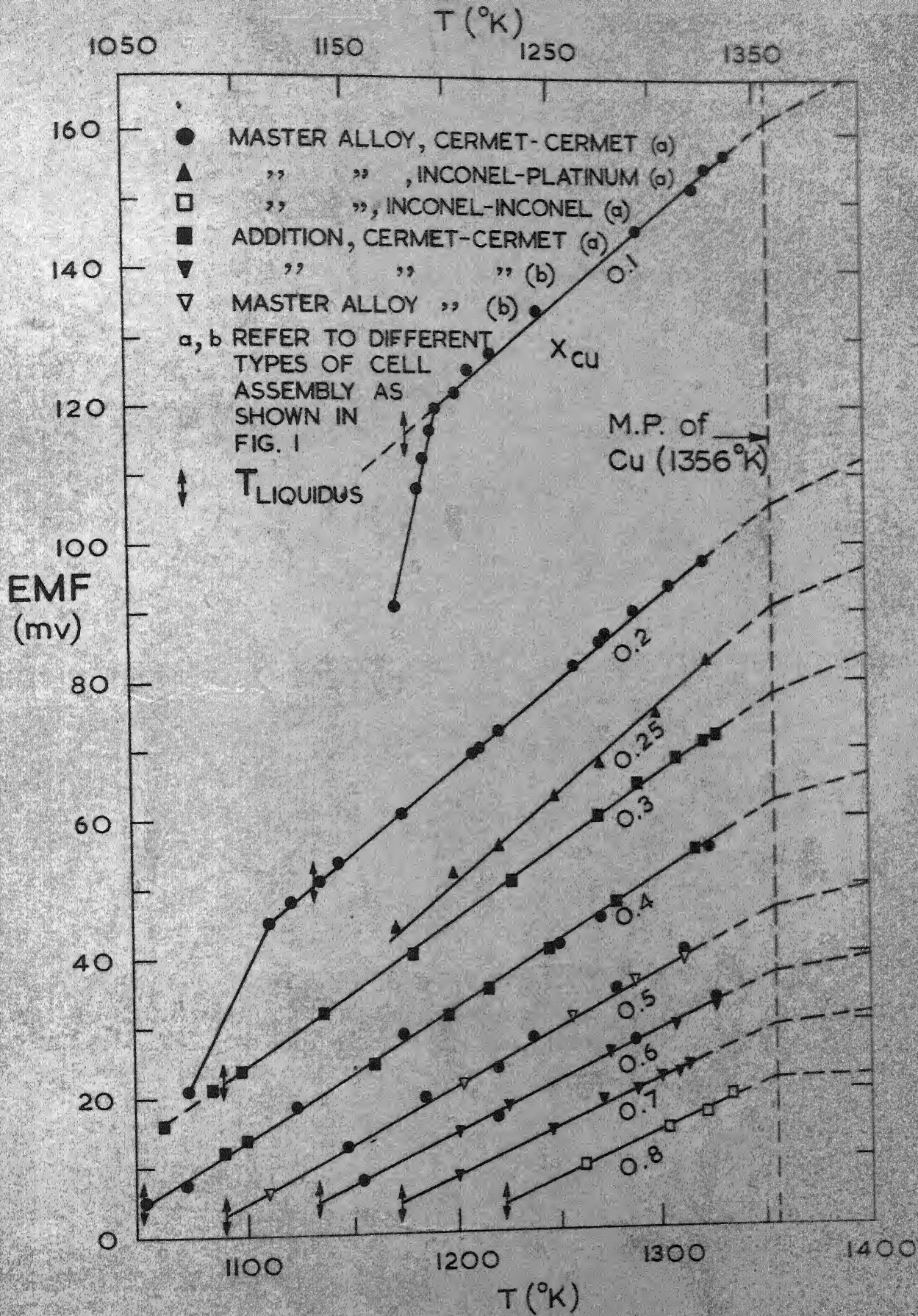


FIG. 2



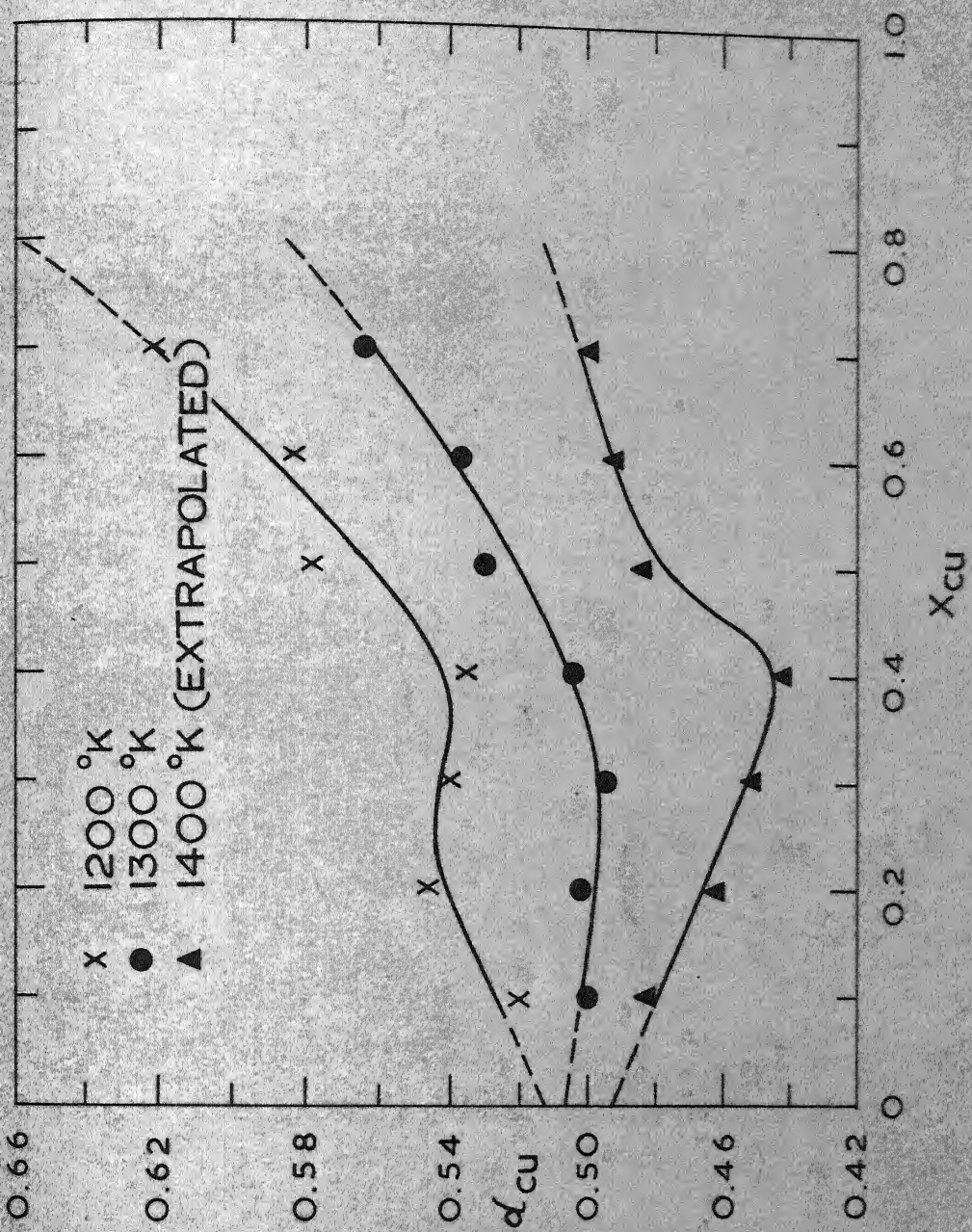


FIG. 4

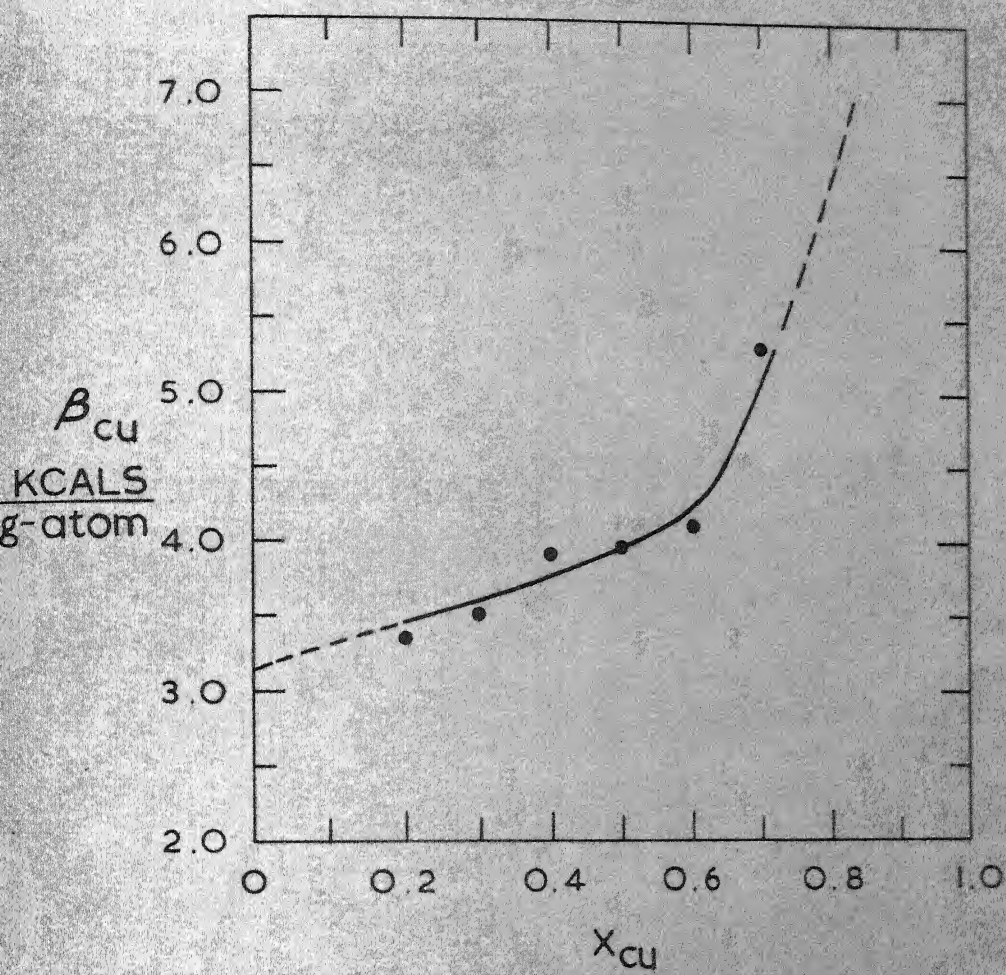


FIG. 5



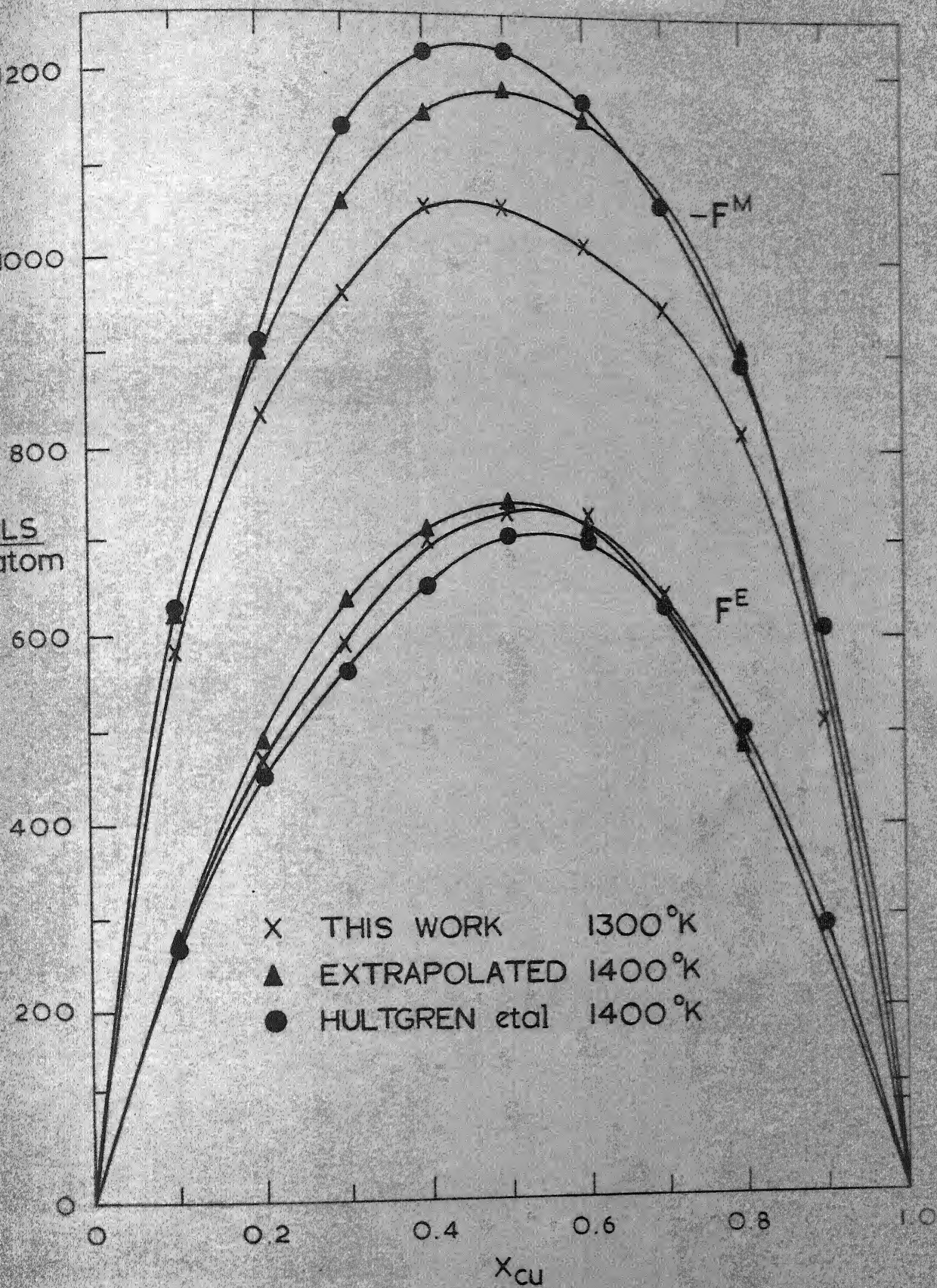


FIG. 6

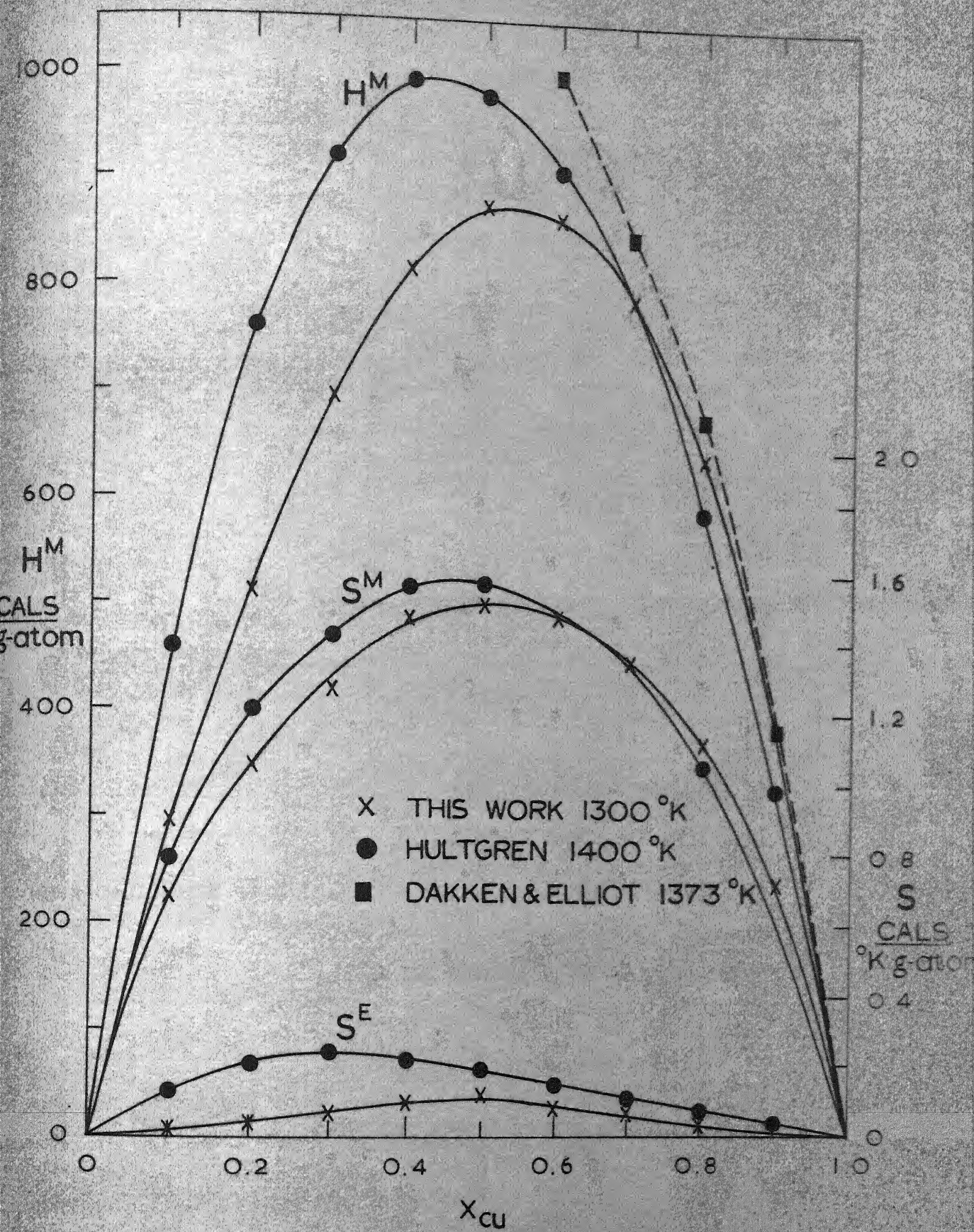
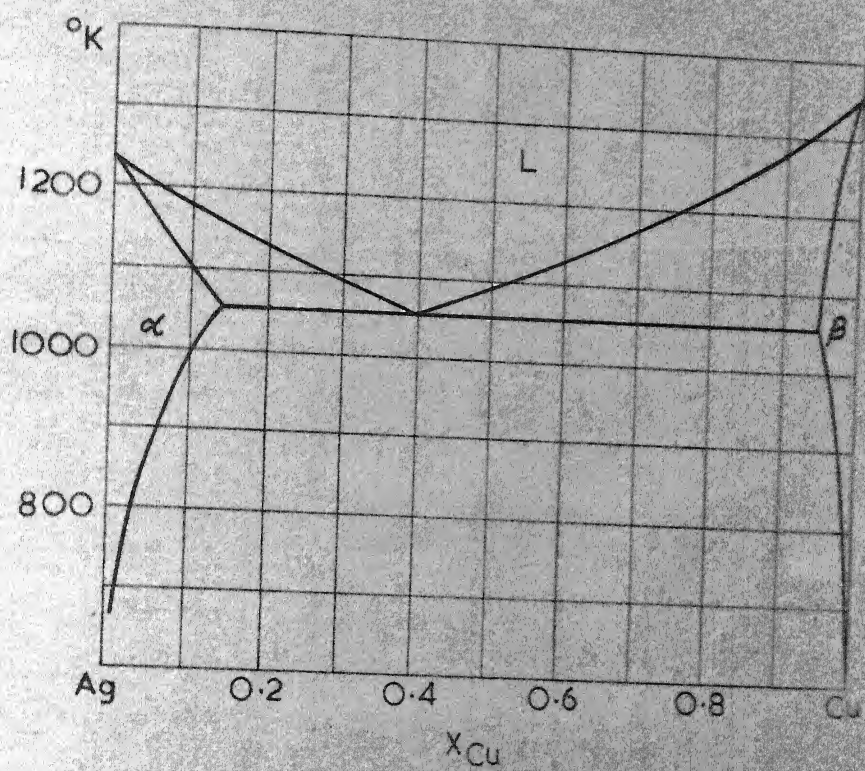


FIG. 7





PHASE DIAGRAM OF COPPER-SILVER SYSTEM

FIG. 8

TABLE I.

Comparison of measured emf values for Calibration Cell Ni-NiO/Cr-Cr<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>/Cu-Cu<sub>2</sub>O  
with the values reported in literature

Temperature (°K)	1173	1232	1273	1116	1150	1200	1323	1153	1020
*This work	264.2	259.2	256.7	260.3	266.3	263.6	255.0	265.6	275.9
Rizzo, Edgwell and Frank	265.6	261.4	258.5	269.6	267.2	263.7	-	267.0	276.5
Charrette and Flengas	264.0	259.9	257.0	268.1	265.7	262.1	253.5	265.4	275.8

\* Experimental values in the order of measurement - This work

\* Calculated values from temperature - Emf relations of the authors

Rizzo, Edgwell and Frank (9.13E) - E = 349.1 - 0.0712 T (°73-1300°K)

Charrette and Flengas (108) - E = 346.68 - 0.07046 T (°927-1328°K)

TABLE II.

Experimental data on Liquid Cu-Ag alloys

$x_{\text{Cu}}$	Temperature range of applicability (°K)	Emf (mV)		Standard deviation (mV)	Maximum deviation (mV)
		$E = -\frac{C+DT}{-C}$	$D$		
0.1	1181-1330	191.1	0.2606	0.7	1.6
0.2	1133-1330	229.4	0.2470	0.6	1.0
0.25	1113-1330	245.6	0.2472	0.9	2.1
0.3	1090-1330	210.6	0.2132	0.4	1.0
0.4	1052-1330	196.6	0.1909	0.4	1.1
0.5	1090-1330	177.8	0.1657	0.6	1.2
0.6	1131-1330	163.8	0.1485	0.4	0.7
0.7	1173-1330	157.6	0.1370	0.5	0.9
0.8	1220-1330	140.4	0.1150	0.8	1.0

1200°K

1300°K  
(# 2c)

$\gamma_{Cu}$	$\gamma_{Cu}^+$ (E)	$\gamma_{Cu}^*$ (E)	$\gamma_{Cu}$ (E)	$\gamma_{Ag}$	$\gamma_{Ag}$	$\gamma_{Cu}$ (E)	$\gamma_{Cu}$	$\gamma_{Cu}$	$\gamma_{Ag}$	$\gamma_{Ag}$
0.1	0.305	0.264	2.640	0.514	1.016	0.268	0.545	2.545	0.512	1.013
0.2	0.523	0.447	2.235	0.846	1.057	0.441	0.415	2.094	0.844	1.055
0.3	0.646	0.552	1.840	0.796	1.122	0.552	0.524	1.737	0.777	1.110
0.4	0.731	0.625	1.563	<b>0.737</b>	<b>1.228</b>	<b>0.692</b>	<b>0.595</b>	<b>1.498</b>	0.719	1.158
0.5	0.816	0.698	1.396	0.686	1.372	0.715	0.675	1.358	0.658	1.316
(E.005)						(E.007)	(E.008)	(E.018)	(E.009)	(E.019)
0.6	0.870	0.744	1.240	0.625	1.573	0.770	0.731	1.215	0.600	1.501
0.7	0.925	0.755	1.141	0.550	1.833	0.927	0.756	1.137	0.524	1.747
0.8	-	-	-	-	-	0.980	0.926	1.045	0.432	2.160

+ Standard state - pure solid copper

\* Standard state - supercooled liquid copper

Table-III (b)

1400°K

Activities in liquid Cu-Ni alloys at 1400°K

$x_{Cu}$	$a_{Cu}^L$	$a_{Cu}^*$ ( $\gamma_{Cu}$ )	$\gamma_{Cu}^+$	$a_{Ni}^L$	$a_{Ni}^*$	$\gamma_{Ni}^+$
0.1	0.246	0.221	2.460	0.510	0.518	1.011
0.2	0.395	0.349	1.575	0.840	0.852	1.050
0.3	0.501	0.469	1.069	0.773	0.770	1.104
0.4	0.578	0.600	1.444	0.715	0.678	1.151
0.5	0.660	0.675	1.321	0.646	0.615	1.202
0.6	0.720	0.739	1.100	0.585	0.552	1.262
0.7	0.775	0.791	1.110	0.509	0.495	1.092
0.8	0.835	0.846	1.043	0.402	0.394	2.010

\* Extrapolated activity values from this work

\* Values reported by Nutgren et al (8)

Table IV.

Thermodynamic functions of mixing at 1300°K in liquid copper-silver alloys

$X_{Cu}$	$-F_{Cu}^M$	$\frac{-F_{Cu}^M}{X_{Cu}}$	$S_{Cu}^{21}$	$\alpha_{Cu}$	$\beta_{Cu}$	$-F_{Ag}^M$	$\frac{F_{Ag}^M}{X_{Ag}}$	$S_{Ag}^M$	$-F^M$	$\frac{F^M}{X^M}$	$S^M$
0.1	3530	*2675	*4.77	0.500	*3310	250	25	0.21	580	295	0.67
		†(1290)									
0.2	2250	2170	3.40	0.502	3390	485	100	0.75	935	510	1.04
0.3	1670	1735	2.62	0.497	3500	660	255	0.70	960	695	1.25
0.4	1335	1415	2.15	0.505	3920	950	455	1.00	1065	815	1.46
0.5	1000	980	1.52	0.579	3950	1125	795	1.46	1065	975	1.50
	(130)	(1240)	(†0.18)	(†0.026)	(†400)	(135)	(†260)	(†0.2)	(†25)	(†190)	(†0.14)
0.6	310	655	1.13	0.583	4100	1320	1130	1.90	1015	765	1.45
0.7	640	480	0.96	0.618	5320	1670	1560	2.50	950	790	1.34
0.8	465	120	0.45	0.490	*6400	2170	2100	3.30	905	660	1.11

\* Extrapolated values from graph

† Experimental values

APPENDIX-ACalibration Run

Run.No.1

Time (hrs)	Temperature °C	Emf (mV)	Variation in emf (mV)
00-23	900	264.2	0.3
23-33	959	259.2	0.4
45-55	1000	256.7	0.2
59-71	943	263.3	0.3
73-84	877	266.3	0.3
86-94	927	263.6	0.2
96-101	1050	255.0	0.5
102-105	949	260.1	0.1
107-110	880	265.6	0.5
121-121	747	275.9	0.4
134-144	731	269.6	0.5
147-155	897	265.2	0.3
157-165	1010	255.3	0.2
169-171	850	269.1	0.3
174-179	700	272	0.6

## Run 2

	$K_{Cu} = 0.7$	Master Alloy	Call 1	Inconel	- Inconel
Time (hrs)	00-03	04-06	07-08	09-11	12-20
Temp. ( $^{\circ}C$ )	1003	977	950	908	780
Time (mv)	17.15	13.5	10.2	5.0	3.2
	36-37	38-46	47-50	51-53	
	1048	1007	912	880	
	24.7	18.7	6.1	3.9	
					21-22
					23-26
					27-30
					31-32
					33-35

### ՀԱՄԱՅՆՈՒՆՆԵՐ

$\delta\text{Cu} = 0.8$	Master Alloy	Cell 7	Inconel - Inconel
Time (hrs)	60-02	04-07	08-13
Temp. ( $^{\circ}\text{C}$ )	1001	1030	1050
$E_{\text{mF}}$ (mv)	11.1	14.5	17.0
		19.2	10.5
		10.5	19.9
		20.9	21.9
			10.2



Run 4  
 Thermal Emf  
 $E = .0313T - 6.25$   
 (800-1000°C)

$K_{Cu} = 0.25$	Master alloy	Cell a	Inconel - Platinum
Time (hrs)	00-03	04-08	10-18
Temp. (°C)	500	527	1000
Emf (mv)	65.8	75.0	52.8
Corrected emf	44.0	52.3	67.8
		63.1	56.7
		56.7	73.1
		75.3	43.6

## Run 5

Master alloy  
 $K_{Cu} = 0.05$ 

Cell a

Cermet - Cermet  
 $K_{Cu} = 0.70$ 

Time (hrs)	00-04	05-06	07-10	08-03	04-06	08-09	10-11	10-18
Temp. (°C)	1041	1088	1050	1025	1007	1117	1097	1030
Emf (mv)	12.8	7.5	14.0	22.7	27.5	25.6	27.8	22.8

Run 6

$X_{Cu} = 0.4$	Master alloy	Cell 1	Cermet - Cermet
Time (hrs)	00-02 03-11 12-14	15-16 17-27	28-33 34-39 41-52 53-56 57-59 61-63
Temp. ( $^{\circ}C$ )	1001 1050 1080	1113 1020	952 952 797 821 903 977
Emf (mv)	95.3 55.5 59.0	64.3 40.3	35.4 14.6 3.5 7.5 26.3 41.5

Run 7

$X_{Cu} = 0.1$	Master alloy	Cell 1	Cermet - Cermet
Time (hrs)	00-04 05-12 14-16 17-20 22-31 32-36		
Temp. ( $^{\circ}C$ )	1050 977 930 1051 939 922		
Emf (mv)	152.5 134.0 122.6 153.2 125.3 121.1		

Run 8 $K_{Cu} = 0.2$ 

Master alloy

Cell a

Cermet - Cermat

Time (hrs)	00-02	03-10	11-13	15-18	19-21	23-25	26-32	33-36	37-40
Temp. (°C)	964	1000	1016	1052	1002	950	912	872	837
Emf (mv)	74.5	85.5	90.0	97.5	86.1	72.8	63.2	53.5	45.3
	42-45	47-49	50-52	53-65	66-69	70-71	72-73		
	901	850	763	938	988	1035	1051		
	21.4	48.2	51.3	66.6	71.9	93.8	97.0		

 $K_{Cu} = 0.3$ Addition

Time (hrs)	77-80	81-83	84-87	88-09	90-114	115-118	119-130	132-135	136-138	139-144	145-148
Temp. (°C)	1054	998	907	925	915	793	964	955	1019	1036	1049
Emf (mv)	71.9	60.4	40.4	23.7	21.9	16.5	32.0	50.9	65.0	69.0	71.4

Run 8 (Contd.) $x_{Cu} = 0.4$  Addition

Time (hrs)	150-152	153-160	162-165	167-69	171-192	184-86	197-190	191-194	195-198	200-202	204-205
Temp. (°C)	1048	1005	943	887	826	799	780	816	923	971	1047
Emf (mV)	55.5	47.7	35.2	24.6	13.8	7.4	5.0	11.8	31.4	40.6	55.2

Run 9 $x_{Cu} = 0.5$  Master alloy Cell a Cermet - Cermet

Time (hrs)	00-03	06-12	14-18	19-22	24-28	29-35
Temp. (°C)	1004	907	837	930	1039	963
Emf (mV)	35.1	20.5	8.0	23.9	40.5	29.9

Run 10
 $x_{Cu} = 0.6$       Master alloy      Cell a      Cermet - Cermet

Time (hrs)	00-04	08-14	16-19	21-23	25-31
Temp. (°C)	1052	979	1013	948	1051
Emf (mV)	33.0	7.5	27.4	16.8	32.9

Run 11
 $x_{Cu} = 0.5$       Master alloy      Cell b       $Cu_2O - Cu_2O$ 

Time (hrs)	00-06	08-11	12-20	22-24	26-29
Temp. (°C)	1039	931	938	985	1015
Emf (mV)	39.4	21.8	6.3	30.9	36.3

Contc.

 $x_{Cu} = 0.6$       Addition      Cell b      Cermet - Cermet

Time (hrs)	34-38	39-42	44-46	48-51	53-64
Temp. (°C)	1035	950	1002	927	1053
Emf (mV)	29.9	18.2	25.6	14.6	33.0

Run 11 (Contd.)

$X_{Cu} = 0.7$  Addition Cell b Cermet - Cermet

Time (hrs)	69-71	72-75	77-82	84-87	89-93	94-95	96-101
Temp. ( $^{\circ}C$ )	1028	999	928	1036	975	1016	1040
Emf (mv)	22.2	18.5	8.0	22.6	14.3	19.9	23.5

Run 12

$X_{Cu} = 0.1$  Master alloy Cell a Cermet - Cermet

Time (hrs)	00-02	04-07	09-14	15-18	20-24	25-28	30-34	36-39	40-48	50-49
Temp. ( $^{\circ}C$ )	1053	949	922	897	1021	972	1064	931	898	912
Emf (mv)	155.0	127.5	120.0	940	146.2	134.0	156.4	122.2	76.5	109

Run 13

$X_{Cu} = 0.9$  Master alloy Cell b Cermet - Cermet

Time (hrs)	00-04	05-07	08-14	16-20	21-28
Temp. ( $^{\circ}C$ )	1027	1056	927	1000	1051
Emf (mv)	7.2	9.25	2.7	2.8	8.4

APPENDIX - B

### APPENDIX - C

#### Preparation of Solid Electrolyte Crucibles:

The crucibles prepared in the laboratory were done by two methods. For both these, starting material is ZIRCOA - B powder containing completely stabilized lime-zirconia solid solution. In the first method, these powders were cold pressed into compacts, sintered at  $1000^{\circ}\text{C}$  for about 6 hrs. and holes were drilled in these. In the second method, slip of suitable consistency was prepared by grinding the ZIRCOA-B powder (- 325 mesh) with water in a pebble mill for one full day. The slip was poured into the plaster of paris moulds and excess amount was drained off after considerable wall thickness of the settled slip was built. The mould was allowed to dry and by slightly tapping, green shapes of crucibles were taken out of the mould. These were initially dried at  $150^{\circ}\text{C}$  and then slowly heated to  $1200^{\circ}\text{C}$ . This initial sintering was done for one full day.

The partially sintered crucibles obtained by these two methods were polished on the outer surface to make it as smooth as possible. These were transferred to gas fired ZIRCOA-B pot furnace for the final sintering. These were arranged on the hearth away from the burner. To avoid the sticking of crucibles to the bottom, zirconia chips were placed below these crucibles. The firing schedule of the furnace was as follows:



Time	A.M.				P.M.			
	8.30	10.30	12	12.30	1	2	2.30	3
Oxygen Pressures PSI	30	40	50	50	60	60	75	80
Acetylene Pressures PSI	4	4	5	5	5	4	4	5
Temperature	R.T.	1200	1425	1525	1700	1900	2000	2000

<u>Cooling Schedule</u>	8.20	8.30	8.45	9	9.15	9.30	10 P.M.
	75	70	65	65	55	45	
	3.75	3	3 $\frac{1}{4}$	3 $\frac{1}{4}$	3 $\frac{1}{4}$	3 $\frac{1}{4}$	
	1950	1850	1750	1700	1600	1550	1375

The furnace was sealed at 10 P.M. and opened <sup>after 18 hrs.</sup> ~~after 10 hrs.~~

Sintered crucibles with densities of 5.5 to 5.9 were obtained.

Note: For a temperature of 2000°C, 70 : 4 or 80 : 4 ( $O_2$  :  $C_2H_2$ ) is recommended. Temperature was measured by an optical pyrometer and was controlled by adjusting the acetylene and oxygen rates. A full oxygen cylinder (1900 PSI) lasts for 2 $\frac{1}{4}$  hrs at 80 PSI. A full acetylene cylinder (260 PSI) lasts for 84 hrs at 5 PSI. With 5 oxygen and 4 acetylene cylinders, temperature can be maintained for maximum of 15 hrs.

## APPENDIX - D

### Estimation of oxygen solubilities in liquid Cu-Ag alloys using Belton and Tankin's model

This model is useful to estimate standard free energies of solution of oxygen in binary alloys from those of the metals. The estimates will be accurate if the solvent metals do not deviate widely from ideal behaviour and the heats of solution of solute in the separate solvent metals do not differ by more than few kilo-calories. Oxygen dissolved is thought to exist as some sort of molecular species. According to this model, solubilities of oxygen in Cu-Ag are estimated as follows:

- (i) Equilibrium partial pressure of oxygen ( $p_{O_2}^0$ ) over pure Cu and  $Cu_2O$  at the desired temperature is calculated.
- (ii) Activity of copper ( $a_{Cu}$ ) corresponding to the desired composition and temperature are noted from the experimental data.
- (iii) Equilibrium  $p_{O_2}$  over  $Ag-Cu(l)$  and  $Cu_2O$  is calculated from the relation

$$p_{O_2}^{1/2} = p_{O_2}^{0/2} / a_{Cu}^2$$

- (iv) Then, standard free energy of solution of oxygen in copper-silver alloys  $F_O^M(Cu-Ag)$  is calculated from the relation derived by Belton and Tankins

$$F_O^M(Cu-Ag) = RT N_{Cu} \ln N_{Cu} + N_{Ag} \ln N_{Ag} - \bar{H}^M + N_{Cu} F_O^M(Cu) + N_{Ag} F_O^M(Ag)$$

where  $\bar{H}^M$  is the measured or calorimetric value.

(a)  $F_O^M$  (Cu) at any temperature can be calculated from Belton and Tankins' (22) value for  $\frac{1}{2} O_2 = \underline{O}$  (Cu) 1 at %

$$F_O^M \text{ (Cu)} = -9930 - 4.75 T \text{ (1150 - 1550}^\circ\text{C)}$$

(b)  $F_O^M$  (Ag) is obtained from Diaz and Richardson's (143) equation for  $\frac{1}{2} O_2 = \underline{O}$  (Cu) 1 at %

$$F_O^M \text{ (Ag)} = -3380 - 5.07 T \text{ (1100}^\circ\text{C)}$$

(v)  $\frac{1}{2} O_2 = \underline{O}$  (Cu - Ag) 1 at %

$$F_O^M \text{ (Cu-Ag)} = -4.576 T \log K$$

K is found out from the above relation

(vi) Also  $K = a_{\underline{O}} / P_{O_2}^{1/2}$

For 1 at % standard state, and reference state as infinitely dilute solution.

$$a_{\underline{O}} = \frac{N_{\underline{O}}}{100} \times 100 = \% \underline{O} \text{ (atm \%)}$$

$$K = \% \underline{O} / P_{O_2}^{1/2}$$

$$\therefore \log \% \underline{O} = -F_O^M \text{ (Cu - Ag)} / 4.576 T + \frac{1}{2} \log P_{O_2}$$

Solubilities at 1200°K and 1300°K were obtained by the above procedure.

$X_{Cu}$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
1200°K	0.75	0.50	0.44	0.54	0.6	0.7	0.76	-
At % O								
1300°K	1.5	0.93	0.90	1.00	0.92	1.04	1.1	0.99

APPENDIX - EUncertainty Analysis:

A typical uncertainty estimate is made for  $X_{Cu} = 0.5$  alloy. As per convention, the uncertainty limit is taken as twice the standard deviation.

Uncertainties in temperature (dT) measurement is due to changes in temperature, thermal gradients and error in thermal calibration. Taking all these into account, dT will not be greater than  $\pm 2^\circ\text{C}$  in the present work.

Standard deviation of emf vs. Temp. plot for  $X_{Cu} = 0.5$  is  $\pm 0.6$  mV.

Hence uncertainty in measured emf =  $\pm 1.2$  mV uncertainties in compositions (d  $X_{Cu}$  or d  $X_{Ag}$ ) are estimated to be not greater than  $\pm .005$ .

$F_{Cu}^M$  reported in the tables is with respect to liquid copper as standard state. Since free energy of fusion is considered to be accurate (error  $< 1\%$ ), change of standard state barely affects the uncertainties in  $F_{Cu}^M$ .

At  $1300^\circ\text{K}$

$$F_{Cu}^M = RT \ln a_{Cu} = -FE$$

$$d F_{Cu}^M = -F \cdot dE \approx 23 \times 1.2 \approx 30 \text{ cal}$$

$$d F_{Cu}^M = RT \frac{d a_{Cu}}{a_{Cu}} + R dT \cdot \ln a_{Cu}$$

$$\therefore d a_{Cu} = \pm .008$$

Percentage wise  $a_{\text{Cu}}$  at  $1300^\circ\text{K}$  for  $X_{\text{Cu}} = 0.5$  is around 1 %.

$$\gamma_{\text{Cu}} = a_{\text{Cu}}/X_{\text{Cu}}$$

$$d \gamma_{\text{Cu}} = \left( \frac{d a_{\text{Cu}}}{X_{\text{Cu}}} \right)^2 + (a_{\text{Cu}} \cdot d X_{\text{Cu}} / X_{\text{Cu}}^2)^2 \\ = \pm .018$$

$$F_{\text{Cu}}^E = RT \ln \gamma_{\text{Cu}} \quad \therefore d F_{\text{Cu}}^E = \pm 35 \text{ cal}$$

$$\alpha_{\text{Cu}} = \log \gamma_{\text{Cu}}/X_{\text{Ag}}^2 \quad \therefore d \alpha_{\text{Cu}} = \pm .02$$

$$S_{\text{Cu}}^M = d F_{\text{Cu}}^M / dT$$

$$(i) \quad d S_{\text{Cu}}^M = d (d F_{\text{Cu}}^M / dT) = 0.15$$

$$(ii) \quad \text{Also } d S_{\text{fusion}} = \pm 0.1$$

$$\text{Hence total uncertainties } d S_{\text{Cu}}^M (\text{total}) = (0.15)^2 + (0.1)^2 = \pm 0.18$$

$$F_{\text{Cu}}^M = F_{\text{Cu}}^M + T S_{\text{Cu}}^M$$

uncertainty in heat of fusion need not be considered because it is taken care of in  $S_{\text{Cu}}^M$  term.

$$\therefore d F_{\text{Cu}}^M = (d F_{\text{Cu}}^M)^2 + (T \cdot d S_{\text{Cu}}^M)^2 = \pm 235 \text{ cal}$$

$$\beta_{\text{Cu}} = F_{\text{Cu}}^M / X_{\text{Ag}}^2 \quad d \beta_{\text{Cu}} = \pm 480 \text{ cal}$$

Similarly uncertainties in  $F_{\text{Ag}}^M$ ,  $H_{\text{Ag}}^M$ ,  $S_{\text{Ag}}^M$ ;  $a_{\text{Ag}}$ ,  $\gamma_{\text{Ag}}$ ;  $F^M$ ,  $H^M$ ,  $S^M$  and  $F^E$ ,  $S^E$  were calculated. These are reported in Table IV.

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